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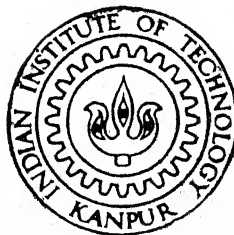
by

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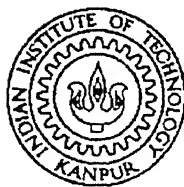
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SANGHAMITRA KAR

to the

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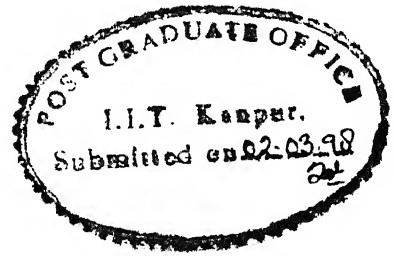
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CERTIFICATE

This is to certify that the work "*Modelling of Ae₃ temperature of steels*" has been carried out by Sanghamitra Kar under our supervision and it has not been submitted elsewhere for a degree.

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Abstract

Prediction of Ae_3 temperature in case of steels is quite important both from the practical as well as theoretical standpoint. Although, in the past several attempts have been made to develop a model to predict the Ae_3 temperature from the composition of the alloys, not a single model is known to be full-proof. Therefore, there still remains the need to establish a model that will predict the Ae_3 temperature as a function of alloy composition as accurately as possible. To this end, the present work is an attempt to model the Ae_3 temperature of low carbon steels based on composition. The alloying elements considered are C, Mn, Si, Ni, Cr, Mo, and Cu. In all, 182 binary and multicomponent data on Ae_3 temperature are considered from different sources. Seven nonlinear binary equations are developed. The predicted Ae_3 temperature for the binary systems is quite close to the experimental value (residue $\leq \pm 1^0$ C). In case of the multicomponent system, a polynomial model is assumed. This model is tested in the following way : keeping the constant term along with the coefficient of the binary terms fixed to that of previously established binary models, the coefficients of the multicomponent terms are evaluated by stepwise linear regression analysis. By doing so, the total error in predicting the Ae_3 temperature is reduced as compared to other available models. The standard error in the present model is 7.34, which is much less compared to earlier models. The model predicts the Ae_3 temperature over a wide range of compositions.

Chapter 1

INTRODUCTION

Steel is an important alloy of iron having multipurpose usage. It is used in most of the engineering applications because of its unique properties like high strength, hardness, toughness, ductility, and corrosion resistance. It has wide applicability owing to its availability and the cost factor. The properties of a typical steel depend on its composition, micro-structure and various heat treatments given to it. Although these processing parameters are interrelated, some of the desired properties can be obtained in a steel purely by proper heat treatment. For this purpose, it is essential to ascertain a priori the austenite to ferrite transformation temperature or the Ae_3 temperature. The Ae_3 temperature varies with compositions and alloying elements present in a steel.

Ae_3 temperature of a steel can be determined experimentally. In industries, steels with wide range of compositions and components are used. Accordingly, the Ae_3 temperature varies. Determination of Ae_3 temperature of each and every steel by experimental means is very inefficient both in terms of cost and time. Many a time it is not possible to carry out experiments. Therefore, efforts have been made to find out an empirical relationship between Ae_3 temperature and compositions of steel. To this end, there are several mathematical models available in the literature but none of them give satisfactory results. The errors in these models are either due to wrong assumptions inherent in the models or the data used to develop the model were erroneous. In some models, the alloying elements considered were very few while in others, the interaction between various alloying elements were not considered. Although the most recent model based on genetic algorithm predicts the Ae_3 temperature satisfactorily, it still suffers from its limited applicability. This is primarily due

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to the use of binary models that were calculated over a narrow range of compositions.

The present work was carried out to develop a mathematical model to predict the Ae_3 temperature in steels based on compositions. In this model, unlike in the previous models, a large number of data were considered. In particular, the number of binary data used in this model is larger than the previous models. Using these binary data, the effect of seven alloying elements namely C, Mn, Si, Ni, Cr, Mo, and Cu on Ae_3 temperature was studied. Respective binary iron–alloys models were developed over a wide range of compositions and all of them were found to be nonlinear. These binary models were adapted in a polynomial model for the multicomponent system and the important multicomponent terms and their coefficients were determined by stepwise linear regression analysis. The results obtained in the present model were statistically analyzed and found to be more accurate compared to existing models in the literature.

Chapter 2

LITERATURE REVIEW

2.1   Binary Phase Diagrams of Iron

A majority of low carbon steels have two-phase structures, namely ferrite and cementite, at room temperature. Heat treatments given to a steel determine the micro-structures and phases present in it, at room temperature. Many properties, like yield strength, ductility, and toughness, are dependent on the micro-structures and phases present in the steel. The knowledge of Ae_3 and Ae_1 temperature of a steel is very helpful for heat treatment. The Ae_3 temperature represents the temperature above which a hypoeutectoid steel shows fully austenitic structure. Similarly, Ae_1 temperature is that temperature where austenite begins to form in a hypoeutectoid steel.

Data on Ae_3 temperature were carefully selected, as in most of the cases the temperature refers to either Ac_3 or Ar_3 temperature. Ac_3 temperature represents the temperature above which fully austenitic structure is obtained while heating and Ar_3 temperature is the temperature below which ferrite begins to form while cooling a hypoeutectoid steel. Thus, Ac_3 temperature lies above Ar_3 temperature, and Ae_3 temperature lies in between these two temperatures. However, it is not necessarily the arithmetic mean of the two [1].

In steels, Fe combines with elements like C, Mo, Si, Cr, and Ni to form commercially important alloys. The alloying elements are classified into two types depending on their effect on phase fields. They are –

1. α stabilizers – These alloying elements expand the α-phase field, e.g., Cr, Mo, and Si.

2. γ stabilizers – The solutes which expand the γ-phase field are known as γ stabilizers,

e.g., Ni, Mn, C, and Co.

Depending on the influence of alloying elements, the phase diagrams are divided into four categories :

- Type 1 *Open γ field* – The alloying elements like Mn, Ni, and Co, expand austenite region towards room temperature and raise the two phase $(\gamma + \delta)$ region towards the melting point (Figure 2.1(a)). Both Ae_3 and Ae_1 temperatures are lowered.

- Type 2 *Expanded γ field* – This is same as Type 1 except that sometimes austenite range is shortened by the formation of iron-rich compounds as shown in Figure 2.1(b). Alloying elements like C, N, Cu, Zn, and Au, belong to this category. The presence of C and N expands the γ field such that the solid solubility of C and N in austenite increases to 2.0 wt.% and 2.8 wt.%, respectively.

- Type 3 *Closed γ field* – The alloying elements of this group restrict the temperature range for stable austenite. Thus, a smaller γ loop and a continuous and wider δ- and α-phase fields are obtained as shown in Figure 2.1(c). Alloying elements belonging to this category are Si, Al, Be, and the carbide forming elements like Cr, Ti, V, Mo, and W.

- Type 4 *Contracted γ field* – In this category, the α- and γ-phase fields are bounded by a miscibility gap, i.e., α and γ solid solutions are in equilibrium with an inter-metallic compound or a solid solution (Figure 2.1(d)). Boron is an important element of this group and other elements are the carbide formers like Ta, Zr, and Nb [2].

The presence of alloying elements in iron affects the phase diagrams in various ways. In order to find their effect on transformation temperature binary iron–alloys phase diagrams were studied. Relevant portions of binary phase diagrams of iron, i.e., Fe–C, Fe–Mn, Fe–Si, Fe–Ni, Fe–Cr, Fe–Mo, and Fe–Cu are given in Figures 2.2 to 2.8, respectively. The phase diagrams are taken from Kubachewski [13].
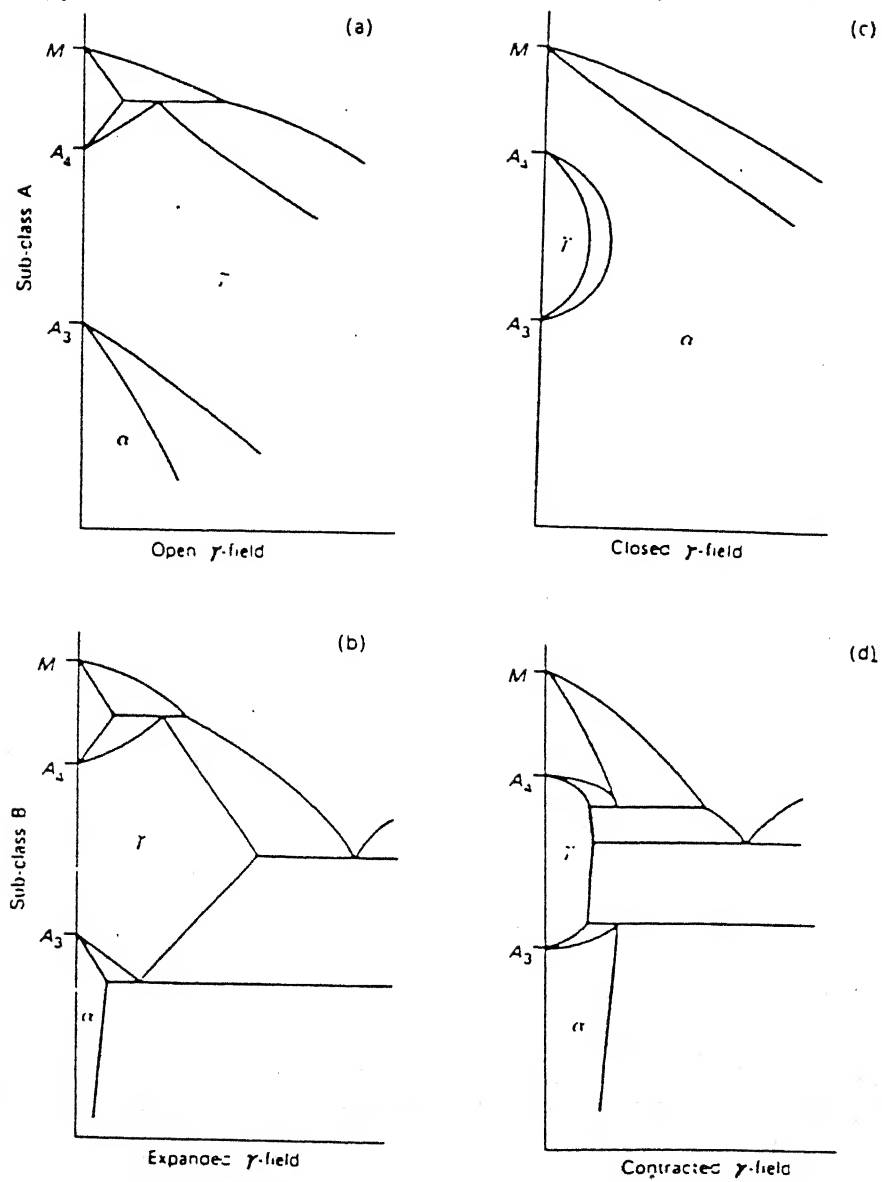
Figure 2.1: Classification of iron-alloys phase diagram : (a) Open γ field, (b) Expanded γ field, (c) Closed γ field, (d) Contracted γ field.
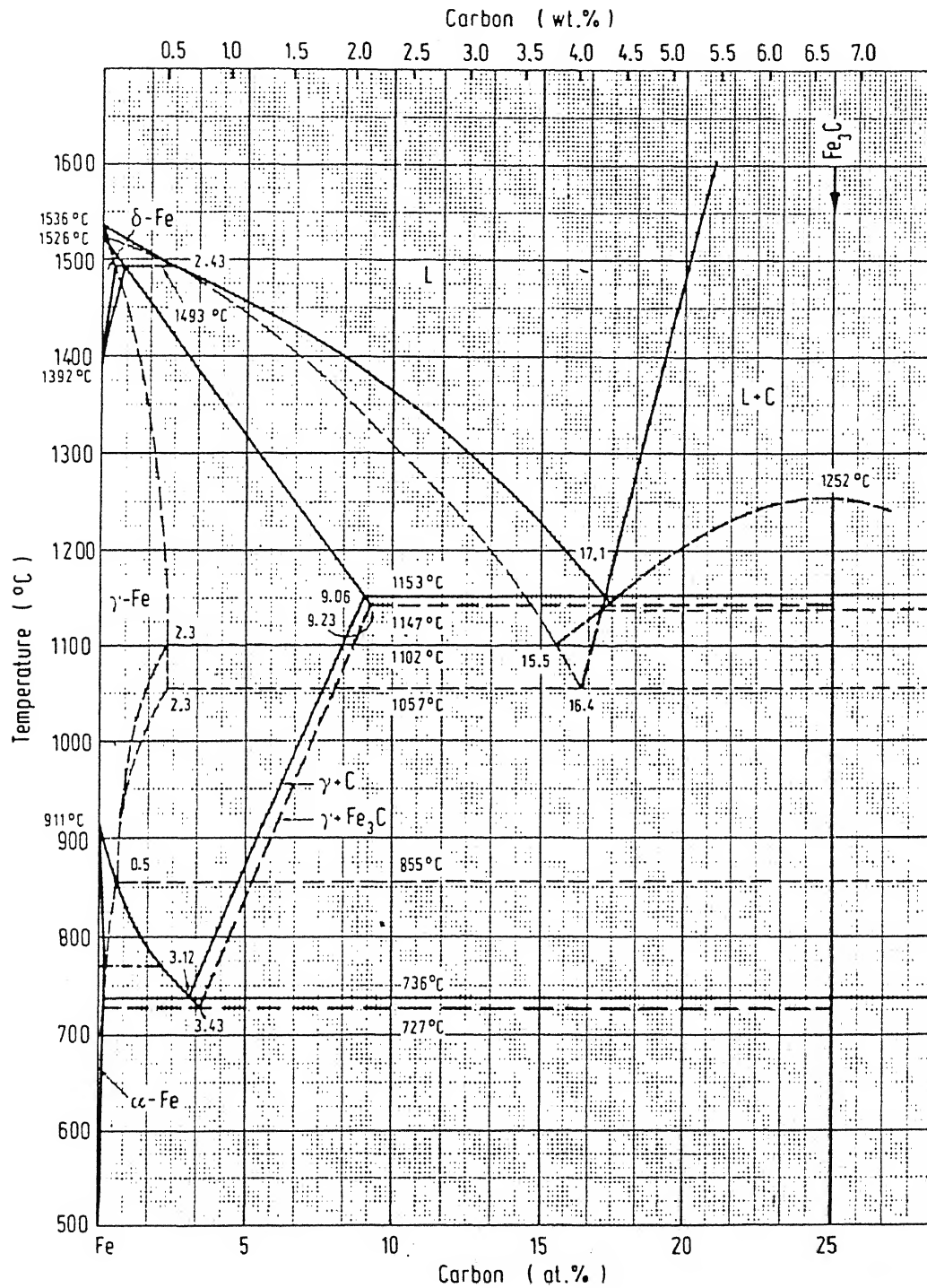
Figure 2.2: Fe–C Phase diagram
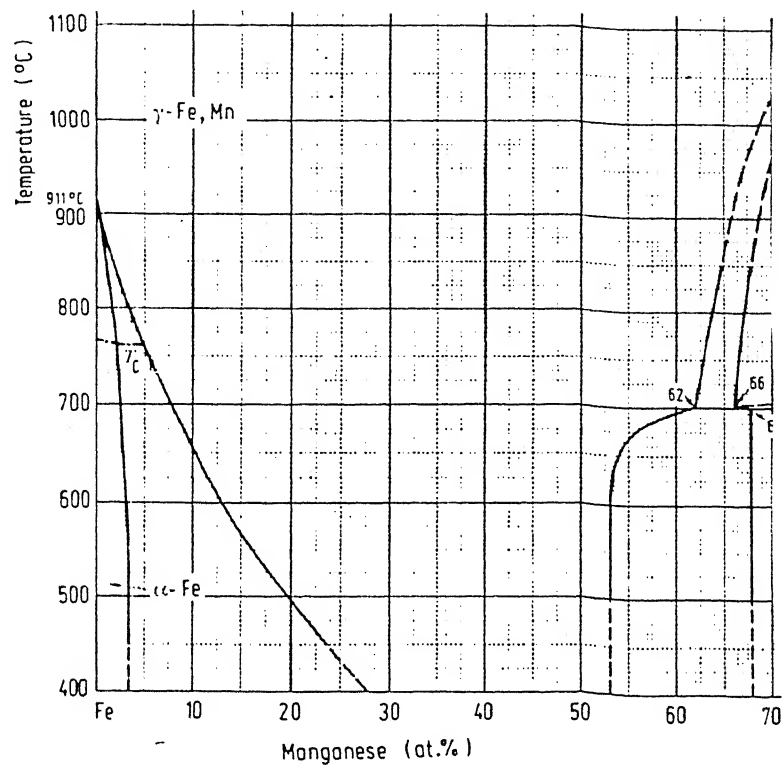
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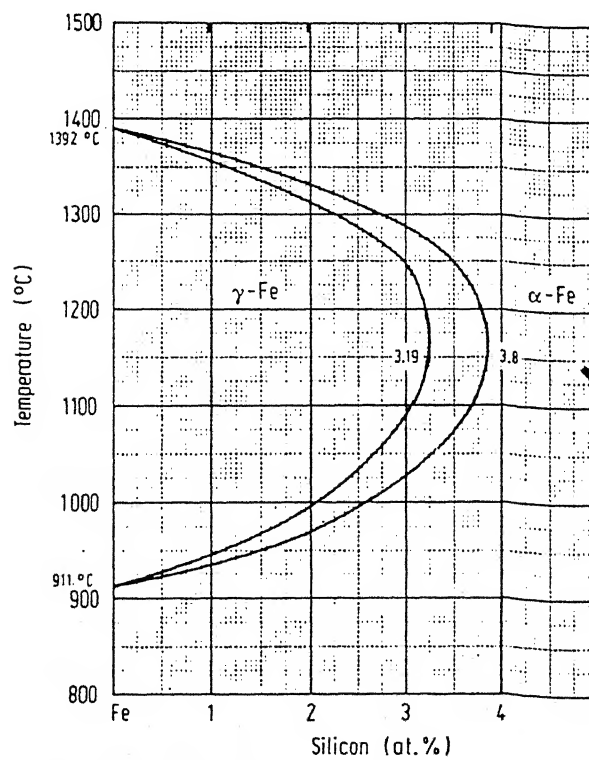
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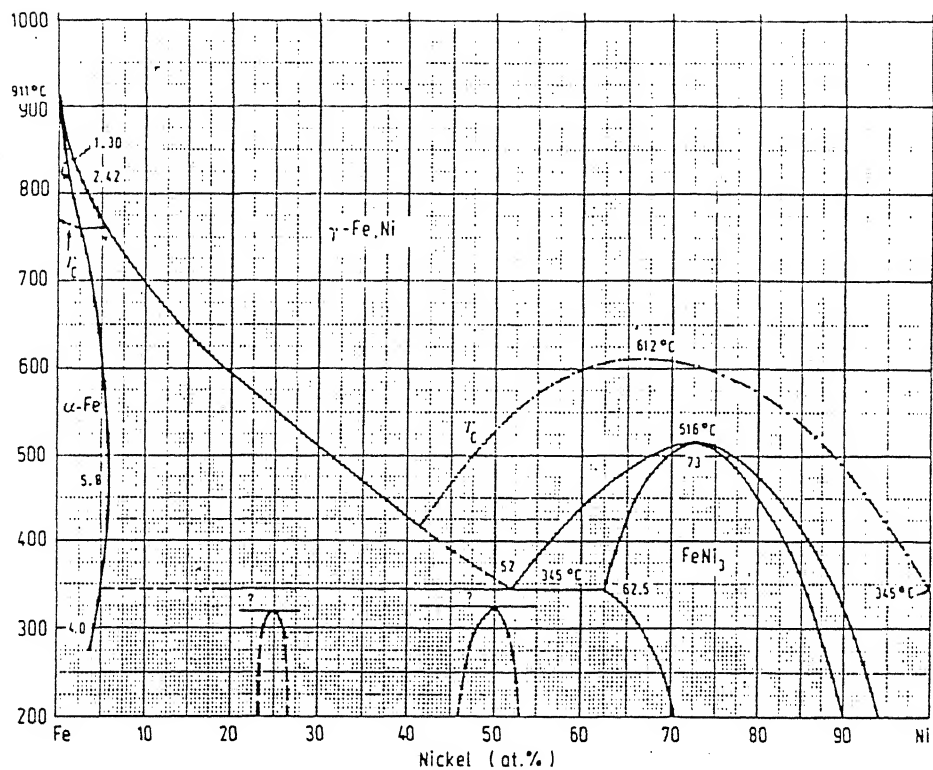
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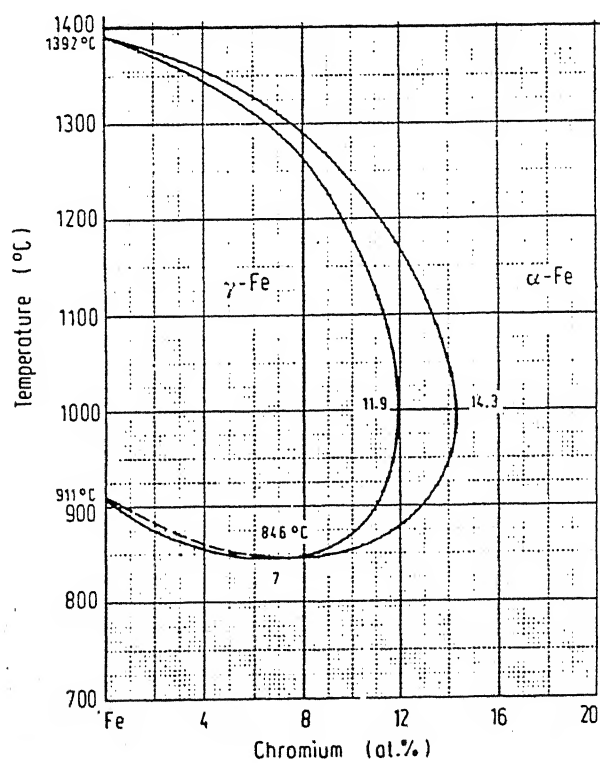
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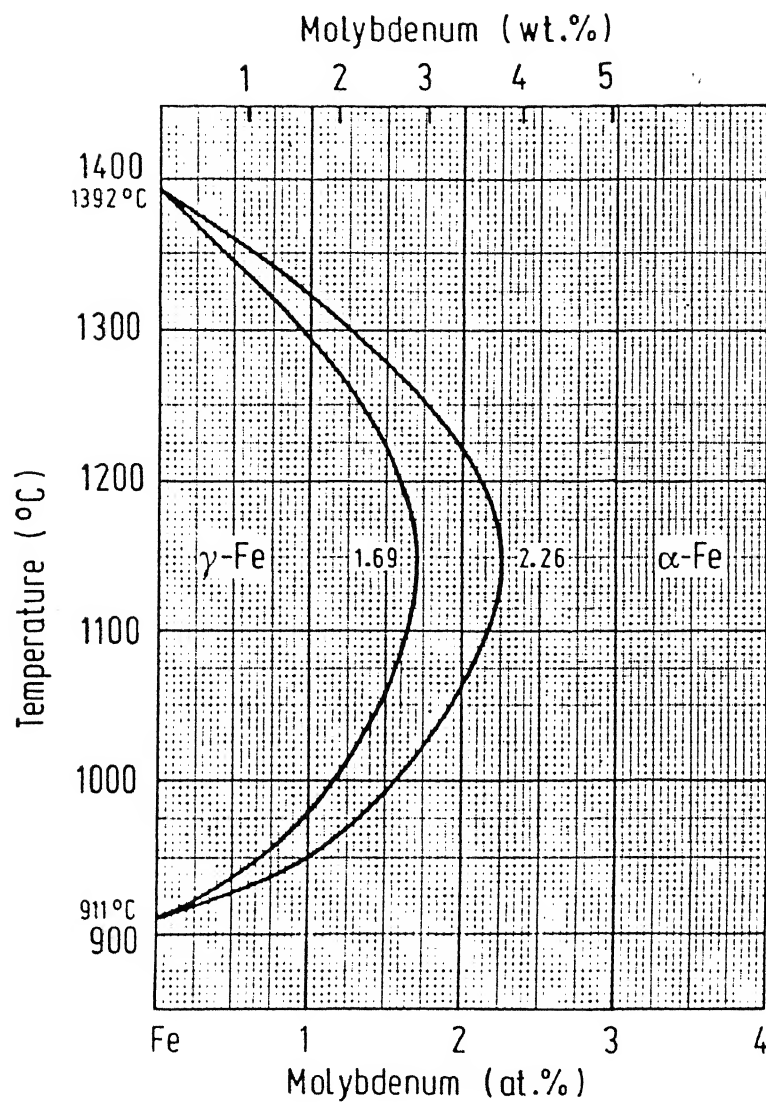
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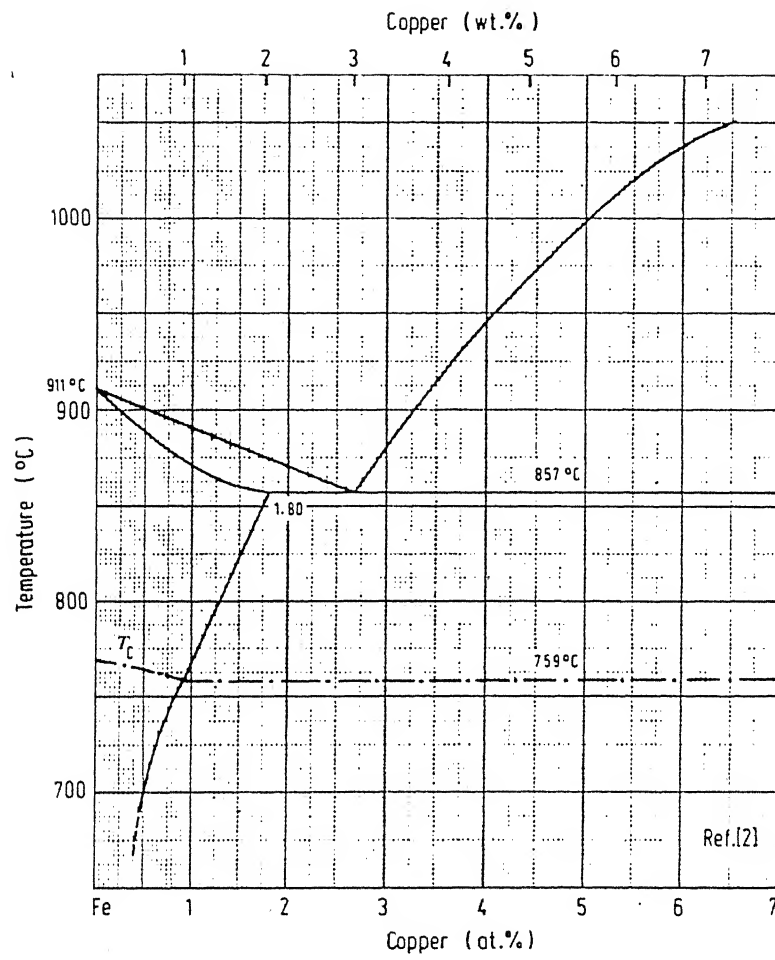
Figure 2.8: Fe–Cu Phase diagram

2.2 Effect of Alloying Elements on Fe–Fe$_3$C Phase Diagrams

The presence of alloying elements changes the critical range of phase stability, the position of eutectoid point, and the location of α- and γ-phase fields as indicated by the binary Fe–Fe$_3$C diagram. The austenite stabilizers lower the eutectoid temperature, thus widening the range of temperature over which austenite is stable. The ferrite stabilizers raise the eutectoid temperature thereby restricting the γ-phase field. Figure 2.9 shows the effect of alloying elements on eutectoid temperature. By proper combination of alloying elements, austenite phase can be obtained at room temperature; as in austenitic stainless steel. Eutectoid carbon composition also changes with presence of alloying elements. All alloying elements tend to decrease the eutectoid carbon content (Figure 2.10) [3]. Usually, no new structural constituents appear, although the composition and proportion of phases present in the steel may be altered considerably [4]. In certain cases, new structural constituents appear, e.g., when Cu exceeds 1% by weight, elemental Cu appears as a second phase.

2.3 Available Data on Ae_3 Temperature

Experimental data for 109 multicomponent steels were collected from different sources. Table 4.2 gives the compositions of steels and their experimental Ae_3 temperature. The first nineteen steels (Sl. No. 1–19) were reported by Grange [5]. The steels were isothermally transformed at a number of temperatures for varying periods extending upto several hours such that the amount of austenite did not change appreciably even by doubling the holding time. The temperature at which the last trace of ferrite transformed to austenite was taken as the Ae_3 temperature.

The United States Steels Corporation [6] has published isothermal transformation diagrams for several steels. Next sixtyseven steels (Sl. No. 20–86) were taken from this source; experimental technique used for determining Ae_3 temperature was same as Grange [5]. The Ae_3 temperature and chemical compositions are taken from the table of Baganis [7].
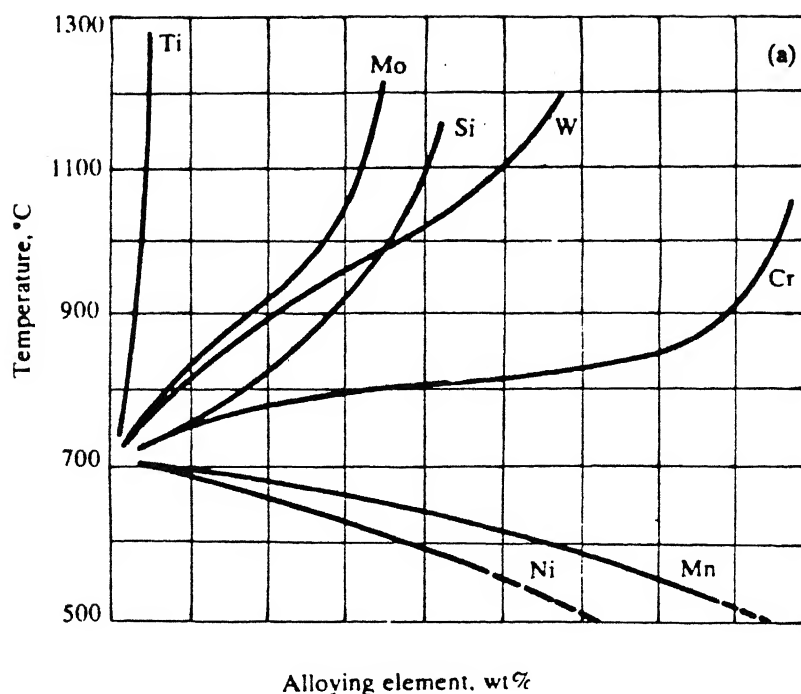
Figure 2.9: Effect of alloying elements on eutectoid temperature

Aaranson and Domian [8] austenitized steels samples (Sl. No. 87-90) at 1300^0C for 15 minutes and quench them to get martensite. The steels were then reheated to temperatures in the vicinity of suspected Ae_3 temperatures and soaked for 15 minutes. The starting structure was fine unstable martensite. So, 15 minutes holding temperature was considered to be adequate for the establishment of equilibrium. The Ae_3 temperature was taken to lie between the highest temperature at which ferrite remained in the micro-structure and the lowest temperature at which it was not present.

Hall et al. [9] homogenized steel samples (Sl. No. 91-95) at 1300^0C for three days. The samples from these steels were then austenitized at 1300^0C for 15 minutes and held isothermally up to 24 hours.

Gilmour et al. [10] reported the data for steels (Sl. No. 96-98). Samples were homogenized at 1200^0C for 18 hours and then quenched in water to get a fully martensitic structure. The samples were then reheated to the holding temperatures, isothermally transformed for three days and quenched in water. Austenite in equilibrium with ferrite was considered to have the holding temperature as its Ae_3 temperature. Austenite composition was determined by micro-probe analysis.
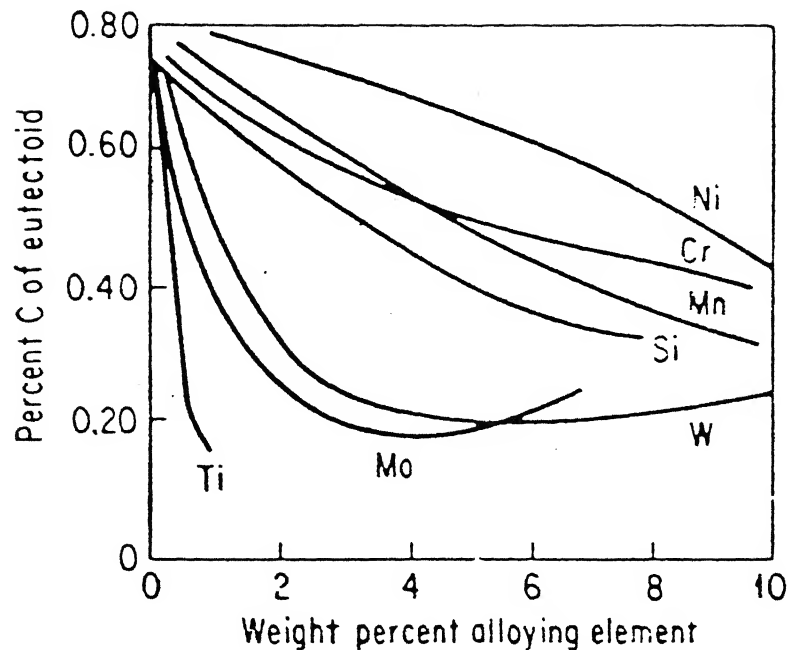
Figure 2.10: Effect of alloying elements on eutectoid carbon content

Kirchner and Uhrenius [11] allowed steel samples (Sl. No. 99-105), which were primarily Fe-Cr-Mn, to isothermally transform during one week to seven months. Austenite in equilibrium with ferrite at a particular isothermal transformation temperature was considered to have the isothermal temperature as its Ae_3 temperature. The composition in this case also was determined by micro-probe analysis. Carbon content of these steels was less than 0.004% and hence assumed to be zero.

Swinden and Woodhead[12] austenitized four Fe-C-Cr steel samples (Sl. No. 106 109) at 1000°C and then allowed isothermal transformation to take place for several hours.

The Ae_3 temperature for binary alloys were taken from the binary phase diagrams given in Kubachewski [13].

Most of the data sources did not report the experimental and instrumental errors separately. Grange [5] had rounded off the results by a maximum of 5°F i.e. 2.8°C. So the error level can be considered to be lower than 2.8°C. No error values were reported in the isothermal transformation diagrams [6]. Aaranson and Domian [8] reported an error value of approximately ±3°C in their data. Hall et al. [9] reported the experimental error to be within ±2°C and Gilmour et al. [10] reported it to be approximately ±1°C. Kirchner et

al. [11] reported an error less than $\pm 0.4^0$C.

2.4 Existing Models for Predicting Ae_3 Temperature

Grange [5] analysed the experimental data for 19 steels containing C, Mn, Si, Ni, Cr, and Mo and suggested the following model for prediction of Ae_3 temperature :

$$T_e(in^0C) = 854.4 - 179.4X_C - 13.9X_{Mn} + 44.4X_{Si} - 17.8X_{Ni} - 1.7X_{Cr} \qquad (2.1)$$

where X represents the weight % of the alloying elements.

Andrews [14] improved the above model by considering few more data and incorporating more alloying elements like Cu, N, V, and P. The equation is :

$$T_e(in^0C) = 913 - \Delta T - 25X_{Mn} - 11X_{Cr} - 20X_{Cu} + 60X_{Si} + 60X_{Mo}$$
$$+40X_N + 100X_V + 700X_P \qquad (2.2)$$

where ΔT accounts for the effects of C and N on Ae_3 temperature. ΔT depends on equivalent carbon content which is obtained by adding one tenth of the weight % of Ni to the weight % of C. The values of ΔT for different equivalent C contents are given in Table 2.1.

Table 2.1: Values of ΔT for Various Equivalent Carbon Content

equivalent C content	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5	0.6	0.7
$\Delta T(^0C)$	24	48	64	80	93	106	117	128	137	145	160	170

Baganis [7] calculated the Ae_3 temperature for different steels using the published data on free energy and activity of binary and ternary alloys of iron. According to him, the equation is :

$$T_e = T_0 + \Delta T \qquad (2.3)$$

where,

$$\Delta T = RT^2 \left(\frac{\sum_{i=2}^{7} X_{i,\gamma}[A - B]}{[C \times D]} \right)$$

$$A = exp\left(\frac{\triangle G_i(T_0)}{RT_0} + E_{1i}X_{1,\gamma}\right)$$

$$B = (1 + e_{1i}X_{1,\gamma})exp\left(\frac{\triangle G_0^0(T_0)}{RT_0} - \frac{e_{11}}{2}(X_{1,\gamma})^2\right)$$

$$C = (1 - X_{1,\gamma})\triangle H_0^0$$

$$D = exp\left(\frac{\triangle G_0^0(T_0)}{RT_0} - \frac{e_{11}}{2}(X_{1,\gamma})^2\right)$$

T_0 = Ae_3 temperature of plain carbon steel.

$X_{1,\gamma}$ = mole fraction of the ith alloying element in γ.

$\triangle G_i^0(T_0)$ = change in the partial molar Gibbs free energy of the ith transformation element at temperature T_0 from ferrite to austenite.

E_{1i} = interaction coefficient for the solute i and carbon in iron.

$\triangle H_0^0$ = change in the partial molar enthalpy of iron for ferrite to austenite transformation.

In the expression for T_e, the suffixes $0, 1, \ldots, i, \ldots, n$ of G, H, and e indicate the constituents, O stands for iron, 1 for carbon and 2 to n for other substitutional alloying elements.

Equations 2.1 and 2.2 contain only linear terms which were obtained by fitting straight lines to the individual binary systems. Khaira [15], Manoj [16] and Arnab [17] considered the self- and mutual-interaction terms. This resulted in considerable decrease in the error in the prediction of Ae_3 temperature. According to Khaira [15] :

$$\begin{aligned} T_e = {} & 910 - 326.73X_C - 32.68X_{Mn} + 45.21X_{Si} - 36.26X_{Ni} + 44.11X_CX_{Mn} \\ & +69.74X_CX_{Ni} - 6.82X_{Cr}^2 + 23.13X_{Mo}^2 - 74.83X_CX_{Si}^2 + 95.69X_{Si}^3 \\ & -9.46X_CX_{Ni}^2 + 214.43X_C^4 - 46.05X_{Si}^4 + 0.11X_{Ni}^4 + 0.17X_{Cr}^4 \\ & -74.46X_CX_{Mo}^3 + 37.37X_C^2X_{Cr}^2 + 8.48X_{Ni}^2X_{Cr}X_{Mo} \end{aligned}$$

(2.4)

According to Manoj [16] :

$$\begin{aligned} T_e = {} & 912 - 423.0X_C - 36.83X_{Mn} + 93.08X_{Si} - 35.68X_{Ni} - 16.78X_{Cr} + 22.17X_{Mo} \\ & -23.618X_{Cu} + 247.6X_C^2 + 83.56X_CX_{Mn} - 124.3X_CX_{Si} + 52.44X_CX_{Ni} \\ & +41.55X_CX_{Cr} - 64.09X_C^2X_{Mn} + 8.541X_{Mn}^2X_{Ni} + 436.4X_{Si}^2X_{Cu} \\ & +5.503X_{Mo}^3 - 13.36X_CX_{Mn}X_{Ni}^2 + 10.05X_CX_{Mn}X_{Ni}X_{Cr} - 64.66X_CX_{Mo}^3 \\ & +0.8889X_{Mn}X_{Ni}^3 - 114.1X_{Mn}X_{Si}X_{Ni}X_{Mo} + 0.0992X_{Mn}X_{Cr}^3 + 8.971X_{Ni}^2X_{Cr}X_{Mo} \end{aligned}$$

(2.5)

According to Arnab [17] :

$$
\begin{aligned}
T_e &= 912 - 660X_C^{0.88} + 454X_C^{1.11} - 38X_{Mn}^{0.92} + 10X_{Si}^{4.38} + 71X_{Si}^{1.13} - 516X_{Ni}^{1.18} \\
&\quad + 468X_{Ni}^{1.22} - 196X_{Cr}^{1.34} + 180X_{Cr}^{1.37} + 1.13X_{Mo}^{4.09} + 29.4X_{Mo}^{1.24} - 24X_{Cu}^{0.96} \\
&\quad + 38.07X_C^{0.4}X_{Mo}^{0.74} + 58.48X_C^{0.33}X_{Ni}^{0.46} - 78.89X_C^{0.32}X_{Si}^{2.04} - 6.54X_C^{0.33}X_{Ni}^{1.47} \\
&\quad - 68.9X_C^{1.47}X_{Mo}^{1.33} + 39.64X_C^{3.30}X_{Cr}^{1.86} + 4.48X_{Ni}^{1.88}X_{Cr}^{1.31}X_{Mo}^{0.59}
\end{aligned}
\tag{2.6}
$$

The terms X_C^2, X_{Mo}^3, etc., represent self-interaction (viz., C–C interaction and Mo–Mo interaction) and terms like $X_C X_{Mo}$ represent mutual-interaction between the elements, where X represents the weight % of the alloying elements. Equations 2.4 and 2.5 were obtained by using stepwise multiple linear regression programs given in IMSL. Equation 2.6 was obtained by using genetic algorithm.

The analysis of results obtained from Equations 2.1 to 2.6 on more than 160 steels of different compositions shows that the standard error is the largest(33^0C) in case of Grange's [5] model (Equation 2.1) and the least(8.9^0C) in case of Manoj's [16] model (Equation 2.5). The coefficient of correlation for Equation 2.6 is approximately 0.991. Equations 2.4 and 2.5 do not converge to the respective binary systems, i.e., when all alloying elements except C are zero, the equation does not reduce to Ae_3 temperature equation of binary Fe–C system. Arnab [17] avoided this problem by forcing binary coefficients into multicomponent model (Equation 2.6).

2.5 Curve Fitting Technique

Curve fitting technique is used to find the influence of independent variables on dependent variable. Regression analysis is the most common tool to handle such kind of problems. The relationship between two variables can be represented by simple algebraic expressions, e.g., polynomials, exponential or logarithmic functions, known as regression function. The regression function involves a set of unknown parameters. Values of parameters, which give the best fit for a given set of data can be obtained by regression analysis. Thus, the relationship between dependent and independent variable is obtained [18, 19].

2.5.1 Linear Regression

When the regression model is linear in parameters (but not necessarily in the independent variables), then the regression model is a linear regression model. Otherwise the model will be a nonlinear regression model [19].

Let a dependent variable y be influenced by p independent variables $x_1, x_2, \ldots, x_p$ and has $p+1$ parameters $b_0, b_1, \ldots, b_p$. Then, the functional relation is :

$$y = f(b_0, b_1, \ldots, b_m, x_1, x_2, \ldots, x_p) \tag{2.7}$$

There are three possibilities :

1. y is linear with respect to both independent variables and parameters, e.g.,

$$y = b_0 + b_1 x_1 + b_2 x_2 + \cdots + b_p x_p \tag{2.8}$$

2. y is linear with respect to parameters, but nonlinear with respect to the independent variables, e.g.,

$$y = b_0 + b_1 x + b_2 x^2 + \cdots + b_p x^p \tag{2.9}$$

3. y is nonlinear with respect to both parameters and independent variables, e.g.,

$$y = ax^b + cx^d \tag{2.10}$$

The first two equations represent linear regression model where as the third equation belongs to nonlinear category. A simple linear regression model is :

$$y_i = \beta_0 + \beta_1 x_i + \epsilon_i \qquad i = 1, 2, \ldots, n \tag{2.11}$$

where the observed values of y_i's constitute the dependent variable, the x_i's are the independent variables, β_0 and β_1 are the intercept and slope parameters, respectively, and ϵ_i's are independently distributed normal errors, each with mean zero and variance σ^2.

2.5.2 Multiple Linear Regression

In multiple linear regression, the dependent variable is regressed on $k(k > 1)$ independent variables. A multiple regression model is :

$$y_i = \beta_0 + \beta_1 x_{i1} + \beta_2 x_{i2} + \cdots + \beta_k x_{ik} + \epsilon_i \qquad i = 1, 2, \ldots, n \tag{2.12}$$

where y_i's represents the dependent variable, x_{i1}'s, x_{i2}'s, ..., x_{ik}'s are the settings of the k independent variables, $\beta_0, \beta_1, \ldots, \beta_k$ are the regression coefficients and ϵ_i's are independently distributed normal errors with mean zero and variance σ^2 [18,19,21].

After deciding the mathematical model, the parameters in the model have to be estimated. Several criteria can be used to estimate the parameters. Least square method is frequently used for this purpose. In least square method, the parameters for which the sum of the squares of the errors (SSE) is minimum, are obtained.

$$SSE = \sum_{i=1}^{n} \epsilon_i^2 = \sum_{i=1}^{n} (Y_i - \hat{Y_i})^2 \qquad (2.13)$$

where, Y_i = observed value, and

$\hat{Y_i}$ = predicted value of Y_i by the equation.

2.5.3 Stepwise Regression

Let Equation 2.12 be the regression model, and $z_1, z_2, \ldots, z_r$ all be function of one or more of the x's, representing the complete set of variables from which the equation is to be choosen. Two opposite criteria for selecting a resultant equation are usually involved :

1. To make the equation useful for predictive purposes the model should include as many z's as possible, so that reliable fitted values can be obtained.

2. To make the evaluation easy, the equation should include as few z's as possible.

The stepwise selection procedure involves insertion of variables until the regression equation is satisfactory. The order of insertion is determined by using the partial correlation coefficient as a measure of the importance of variables not yet in the equation. Initially, the z having the highest correlation coefficient with Y is entered into the equation. The significance of the variable is then tested. In the next step, the partial correlation coefficients of all the predictors not in the models is calculated, and the z having the highest value is entered into the model. The overall regression is now checked for the significance, the improvement in R^2 value is noted and the partial F-values for both the variables in the equation are examined. The lower of the two partial F's is then compared, and the corresponding predictor variable is retained in the equation or rejected, according to whether the test is significant or not. A predictor that may have been the best entry candidate at an earlier stage, may

at stage, be superfluous because of the relationships between it and other variables, now in the regression. To check on this, the partial F criterion for each variable in the regression at any stage of calculation is evaluated. The process of adding and dropping of predictors continues till no further addition or dropping of variables into or from the model, occurs.

The α values used for the partial F-test, represents the significance level. One can select different values of α for entering into or leaving from the model. α_{entry} is always kept less than α_{exit}, and it is usually the best to set $\alpha_{entry} = \alpha_{exit}$ [18].

2.6 Scope of Present Work

All models discussed in section 2.4 have certain drawbacks. This could be due to certain assumptions in deriving the models. For example, the linear dependence of Ae_3 temperature on composition by Grange [5] ignored both self- and mutual-interaction of the alloying elements. Andrews [14] improved the Grange's model [5] by considering self-interaction of C and Ni and mutual-interaction between them. But, the interaction terms of other alloying elements were ignored. His model was not accurate for steels having Mn>1.0% and Si>0.8% by weight, as the interaction terms become important in these steels. Baganis [7] considered the equilibrium between ferrite and austenite in his model and used thermodynamic data of binary and ternary alloys of iron for calculation. Self-interaction of C and its interaction with other alloying elements were taken into account in his model. Self- and mutual-interactions of alloying elements other than C, were ignored. His model failed to predict the Ae_3 temperature, in case of high alloy steels. Baganis's model (Equation 2.3) also suffers from the criticism that it is very complicated and that it involves too many thermodynamic data which are not readily available.

Some of the above drawbacks were overcome in Khaira's [15] and Manoj's [16] models (Equations 2.4 and 2.5). They considered all possible self- and mutual-interactions among the alloying elements. In their model, the root mean square error was reduced to 8.9^0C, which was considerably low in comparison to Grange's [5] and Andrew's [14] models (Equations 2.1 and 2.2). But, Khaira's [15] and Manoj's [16] model do not predict the Ae_3 temperature of the binary iron alloys. On the other hand, Arnab's [17] model (Equation 2.6) predicts the Ae_3 temperature quite well for the same system, but only within a small range of composition. The root mean square error of 9.5^0C as associated with his model is marginally higher than

that of Manoj's [16] and Khaira's [15] models.

The present work is carried out with a view to develop a model that would predict the Ae_3 temperature-very close to the experimental value. In this context, a polynomial model for the multicomponent system is assumed. The effect of seven alloying elements, namely C, Mn, Si, Ni, Cr, Mo, and Cu, on Ae_3 temperature of steel is studied individually. Seven binary models are obtained considering the composition of each alloying elements over a wide range. These binary models are then incorporated in the polynomial model, replacing the binary terms present in it. The constant term takes the value of transformation temperature for pure iron. The remaining mutually interacting terms in the multicomponent model are determined by stepwise multiple linear regression analysis. The performance of this model is found to be statistically better than that of existing models in the literature.

Chapter 3

MODEL FOR BINARY ALLOYS OF IRON

3.1 Selection of Binary Data and Regression Model

The binary data is taken from the binary phase diagrams given in Kubachewski [13]. Manoj [16] and Arnab [17] calculated the binary iron-alloys equations considering alloying elements over a small range of compositions. The nonlinear models developed by Arnab [17] have two advantages over linear models developed by Manoj [16], namely, greater accuracy in calculation and lesser number of terms in the model. But, these models do not give satisfactory result when the composition of an alloying element goes beyond the range over which the equation was developed. Since, the binary models are forced into the multicomponent model, they should give satisfactory result over the entire range of composition for a particular alloying element present in multicomponent steels. Hence, in the present work the binary equations are recalculated by taking the binary data over the entire range of composition, present in multicomponent steels. Table 3.1 shows the maximum and minimum composition of an alloying element in multicomponent steels and binary alloys.

The nonlinear model used for all the binary systems is :

$$Y = a_0 + a_1 x^{b_1} + a_2 x^{b_2} \tag{3.1}$$

where, Y = dependent variable

x = independent variable

and the values of a_0, a_1, a_2, b_1, and b_2 can be determined by doing nonlinear regression on

21

Table 3.1: Range of compositions of various alloying elements

Elements		C	Mn	Si	Ni	Cr	Mo	Cu
multicomponent	min. comp.(in wt.%)	0	0	0	0	0	0	0
steels	max. comp.(in wt.%)	0.68	5.01	1.83	5.00	5.70	0.83	1.49
binary	min. comp.(in wt.%)	0	0	0	0	0	0	0
steels	max. comp.(in wt.%)	0.77	5.91	1.53	5.77	6.54	2.72	3.40

known values of x and Y data [22]. Various statistical analysis are then carried out for the evaluation of results. Some of the statistical parameters used in this contexts are described below :

- **Standard error of estimate** : It is also called as standard deviation of estimate and is defined as –

$$SE = \left[\frac{\sum\limits_{}^{n}(Y_i - \hat{Y_i})^2}{n} \right]^{\frac{1}{2}} \tag{3.2}$$

- **Residue of error estimate** : It is the difference in the experimental and predicted values of a dependent variable.

$$\text{Residue } = Y_i - \hat{Y_i} \tag{3.3}$$

- **Sum of the squared residue** : It is the sum of the square of the errors or residues.

$$SSE = \sum\limits_{}^{n}(Y_i - \hat{Y_i})^2 \tag{3.4}$$

3.2   Determination of Analytical Expression for Ae_3 Temperature in Binary Iron-Alloy Systems

The equation of Ae_3 temperature for binary iron-alloy system is represented as :

$$T_e = a_0 + a_1 x^{b_1} + a_2 x^{b_2} \tag{3.5}$$

where, T_e = experimental Ae_3 temperature

x = weight fraction of alloying element

In each model, a_0 is taken to be 912^0C, the austenite to ferrite transformation temperature and, the values of a_1, a_2, b_1, and b_2 are determined by using a standard routine (E04FCF) available in NAG FORTRAN library. The above model involves four unknowns, therefore, instead of obtaining a unique solution, a set of solutions are obtained. Each set of the solutions is again tested by using a standard curve fitting software package PEAKFIT. The result having best fit and minimum standard error is accepted. In some cases, e.g., Fe–Mn, Fe–Ni, and Fe–Cu, the values of a_2 and b_2 are found to be very low, and hence they are neglected. By doing so, the accuracy of the result is found to be unaffected. Thus, for some cases, the equation becomes :

$$T_e = a_0 + a_1 x^{b_1} \qquad\qquad (3.6)$$

Table 3.2: The binary models coefficients when x is in weight fraction

System	a_0	a_1	b_1	a_2	b_2
Fe–C	912	-37979.04	0.88	75345.25	1.11
Fe–Mn	912	-1867.0	0.83	0	0
Fe–Si	912	10^9	3.92	8509	1.05
Fe–Ni	912	-884.88	0.62	0	0
Fe–Cr	912	11730.51	1.70	-4031.96	1.14
Fe–Mo	912	1.6×10^8	3.99	3818	1.05
Fe–Cu	912	-1415.32	0.97	0	0

Table 3.2 shows the values of parameters for binary iron-alloys systems, when x is expressed in weight fraction of the alloying elements. Table 3.3 shows these values, when x is expressed in weight % of the alloying elements. Table 3.4 shows the experimental and predicted Ae_3 temperature along with the composition of alloying elements and residues. The residue is found to be lesser than that in the existing binary models.

Table 3.3: The binary model coefficients when x is in weight %

System	a_0	a_1	b_1	a_2	b_2
Fe–C	912	-660	0.88	454	1.11
Fe–Mn	912	-40.84	0.83	0	0
Fe–Si	912	14.45	3.92	67.6	1.05
Fe–Ni	912	-50.92	0.62	0	0
Fe–Cr	912	4.67	1.70	-21.16	1.14
Fe–Mo	912	1.67	3.99	30.0	1.05
Fe–Cu	912	-16.25	0.97	0	0

Table 3.4: Predicted Ae_3 temperature and residues in binary models

System	Weight% of alloying element	Experimental Ae_3 temperature	Predicted Ae_3 temperature	Residue
Fe–C	0.00	912.00	912.00	0.00
	0.05	882.00	881.05	0.95
	0.11	856.00	856.56	-0.56
	0.18	834.00	833.73	0.27
	0.25	815.00	814.58	0.42
	0.33	795.00	795.83	-0.83
	0.40	782.00	781.50	0.50
	0.47	769.00	768.76	0.24
	0.55	756.00	755.81	0.19
	0.60	749.00	748.48	0.52
	0.66	740.00	740.38	-0.38
	0.70	736.00	735.37	0.63
	0.77	727.00	727.28	-0.28

Table3.4 : Continued

System	Weight% of alloying element	Experimental Ae_3 temperature	Predicted Ae_3 temperature	Residue
Fe–Mn	0.00	912.00	912.00	0.00
	0.49	890.00	889.41	0.59
	1.48	856.00	855.45	0.55
	1.97	840.00	840.30	-0.30
	2.46	826.00	825.79	0.21
	2.95	811.00	811.76	-0.76
	3.44	798.00	798.12	-0.12
	3.94	785.00	784.55	0.45
	4.43	771.00	771.52	-0.52
	4.92	759.00	758.74	0.26
	5.42	746.00	745.92	0.08
	5.91	734.00	733.56	0.44
Fe–Si	0.00	912.00	912.00	0.00
	0.13	920.00	919.94	0.06
	0.25	927.00	927.83	-0.83
	0.38	936.00	936.80	-0.80
	0.51	946.00	946.37	-0.37
	0.63	956.00	955.98	0.02
	0.76	968.00	967.60	0.40
	0.89	980.00	980.97	-0.97
	1.02	996.00	996.64	-0.64
	1.14	1013.00	1013.72	-0.72
	1.27	1035.00	1035.76	-0.76
	1.53	1094.00	1094.19	-0.19

Table3.4 : Continued

System	Weight% of alloying element	Experimental Ae_3 temperature	Predicted Ae_3 temperature	Residue
Fe–Ni	0.00	912.00	912.00	0.00
	0.53	878.00	877.65	0.35
	1.05	860.00	859.52	0.48
	1.58	845.00	844.38	0.62
	2.10	831.00	831.34	-0.34
	2.62	819.00	819.48	-0.48
	3.15	809.00	808.29	0.71
	3.67	798.00	797.98	0.02
	4.20	789.00	788.03	0.97
	5.24	770.00	769.81	0.19
	5.77	761.00	761.06	-0.06
Fe–Cr	0.00	912.00	912.00	0.00
	0.37	906.00	906.05	-0.05
	0.93	896.00	896.65	-0.65
	1.86	883.00	882.48	0.52
	2.80	870.00	870.45	-0.45
	3.73	860.00	860.88	-0.88
	4.67	854.00	853.53	0.47
	5.61	849.00	848.49	0.51
	6.55	846.00	845.69	0.31
	7.49	845.00	845.10	-0.10

Table3.4 : Continued

System	Weight% of alloying element	Experimental Ae_3 temperature	Predicted Ae_3 temperature	Residue
Fe–Mo	0.00	912.00	912.00	0.00
	0.34	921.00	921.78	-0.78
	0.69	933.00	932.90	0.10
	1.03	945.00	945.13	-0.13
	1.37	961.00	960.03	0.97
	1.71	979.00	979.42	-0.42
	2.04	1005.00	1004.77	0.23
	2.38	1040.00	1040.43	-0.43
	2.55	1063.00	1062.92	0.08
	2.72	1089.00	1089.14	-0.14
Fe–Cu	0.00	912.00	912.00	0.00
	0.26	907.00	907.60	-0.60
	0.53	903.00	903.22	-0.22
	0.92	897.00	897.01	-0.01
	1.05	895.00	894.96	0.04
	1.31	891.00	890.88	0.12
	1.57	887.00	886.83	0.17
	1.84	883.00	882.64	0.36
	2.62	871.00	870.64	0.36
	2.88	867.00	866.66	0.34
	3.40	858.00	858.74	-0.74

3.3 Assessment of Models

Table 3.5 shows the values of different statistical parameters described in section 3.1. The values indicate excellent reliability of models. The standard error in each case is found to be very small. Mean residue in most of the cases lies within ± 0.08. Binary models for Fe–Mn, Fe–Ni, and Fe–Cu individually contain only two terms, but the other four models have three terms each. Small number of terms makes the equation easy to evaluate. In all the models,

the absolute value of residue is less than 1.00. A good agreement between experimental value and predicted value can be seen in Figures 3.1 to 3.7.

Table 3.5: Statistical analysis of the results in binary models

System	No. of data points(n)	SSE	Mean of Residue	Maximum Residue (absolute)	SE	Correlation coefficient
Fe–C	13	3.39	0.13	0.95	0.51	0.9999624
Fe–Mn	12	2.12	0.07	0.76	0.42	0.9999708
Fe–Si	12	4.11	-0.40	0.83	0.59	0.9999667
Fe–Ni	11	2.57	0.22	0.71	0.48	0.9999527
Fe–Cr	10	2.26	-0.03	0.88	0.48	0.9998191
Fe–Mo	10	2.02	-0.05	0.78	0.45	0.9999709
Fe–Cu	11	1.38	-0.02	0.74	0.35	0.9997717
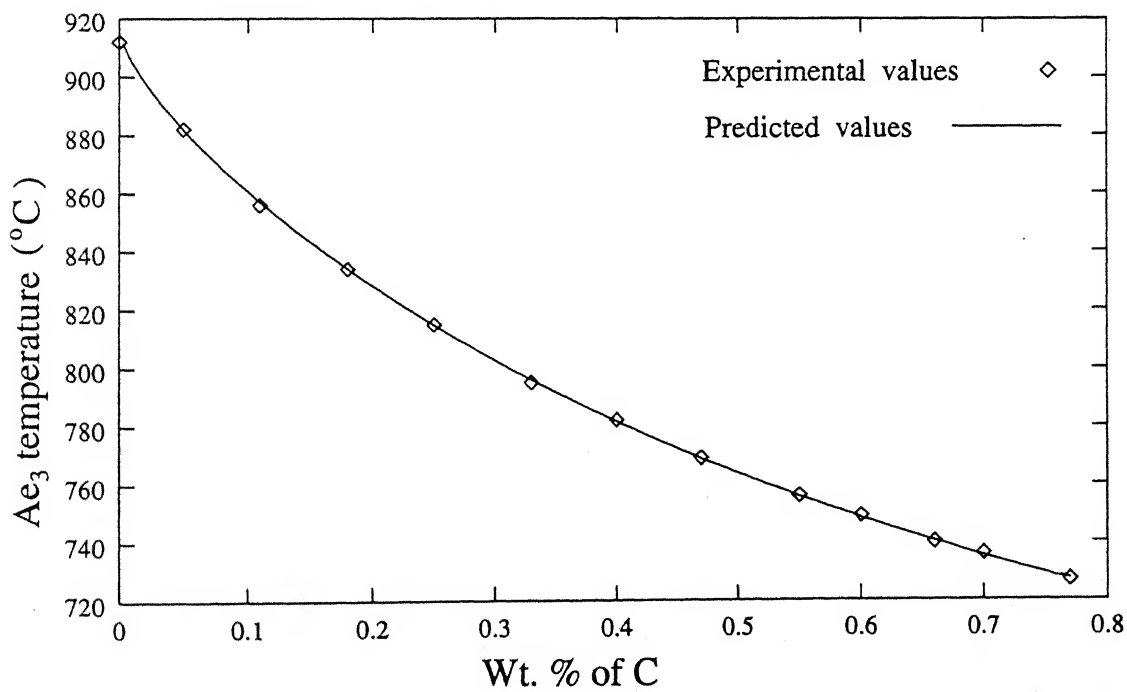
Figure 3.1: Experimental data and predicted Ae_3 temperature profile of Fe–C system
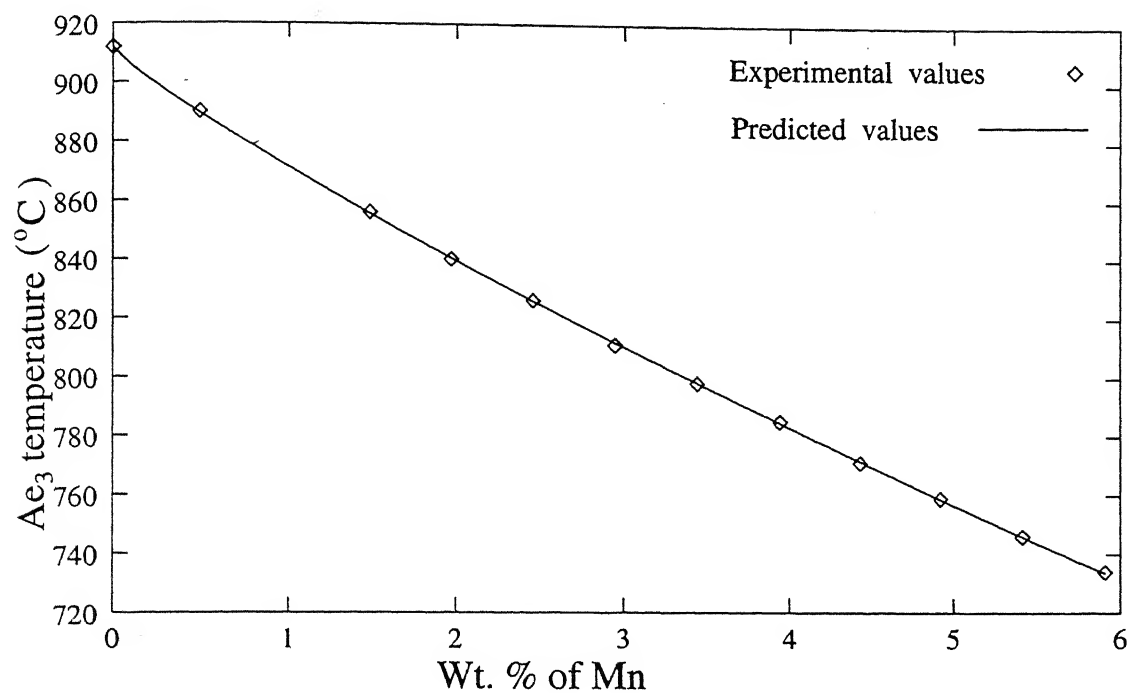
Figure 3.2: Experimental data and predicted Ae_3 temperature profile of Fe–Mn system
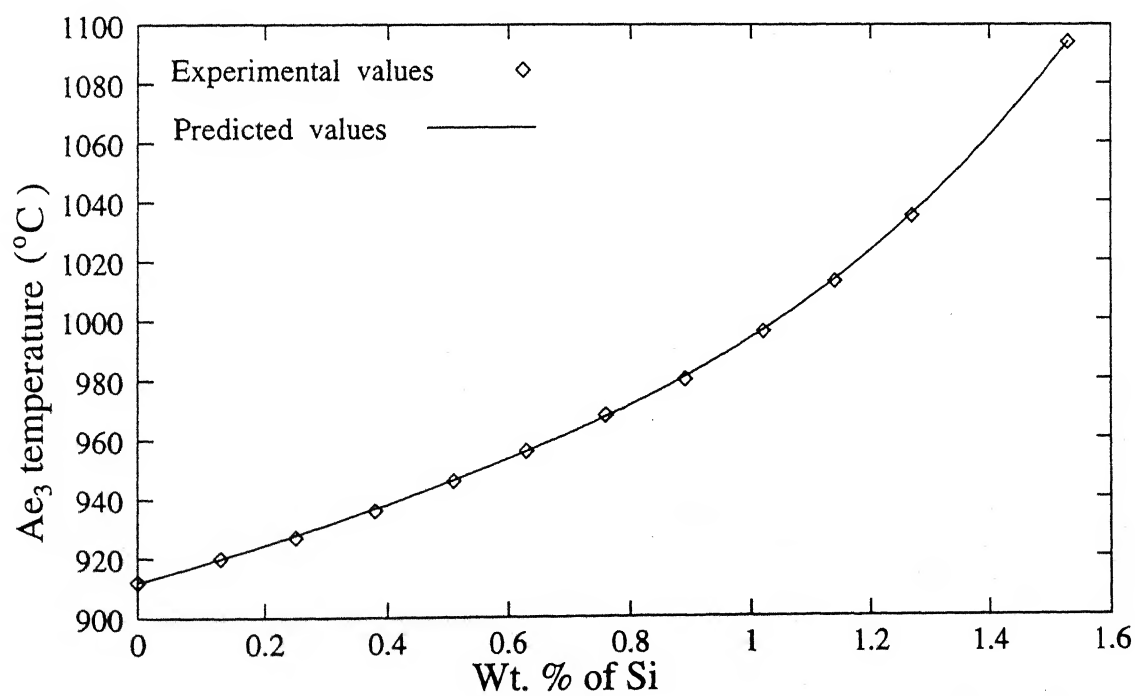
Figure 3.3: Experimental data and predicted Ae_3 temperature profile of Fe–Si system
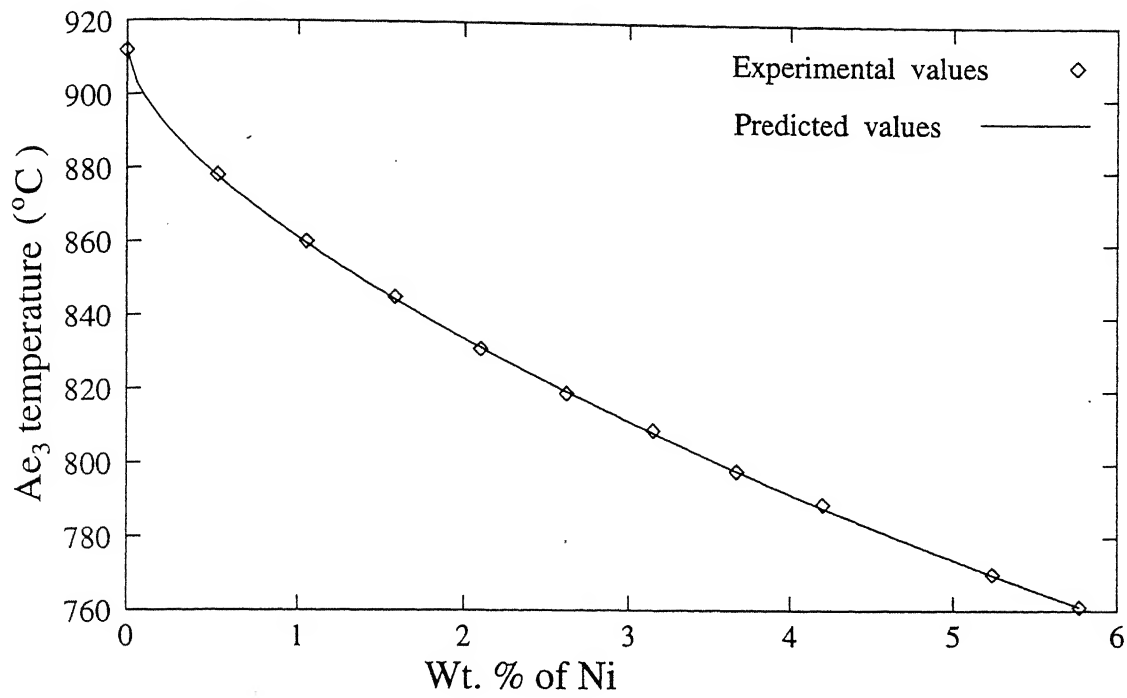
Figure 3.4: Experimental data and predicted Ae_3 temperature profile of Fe–Ni system
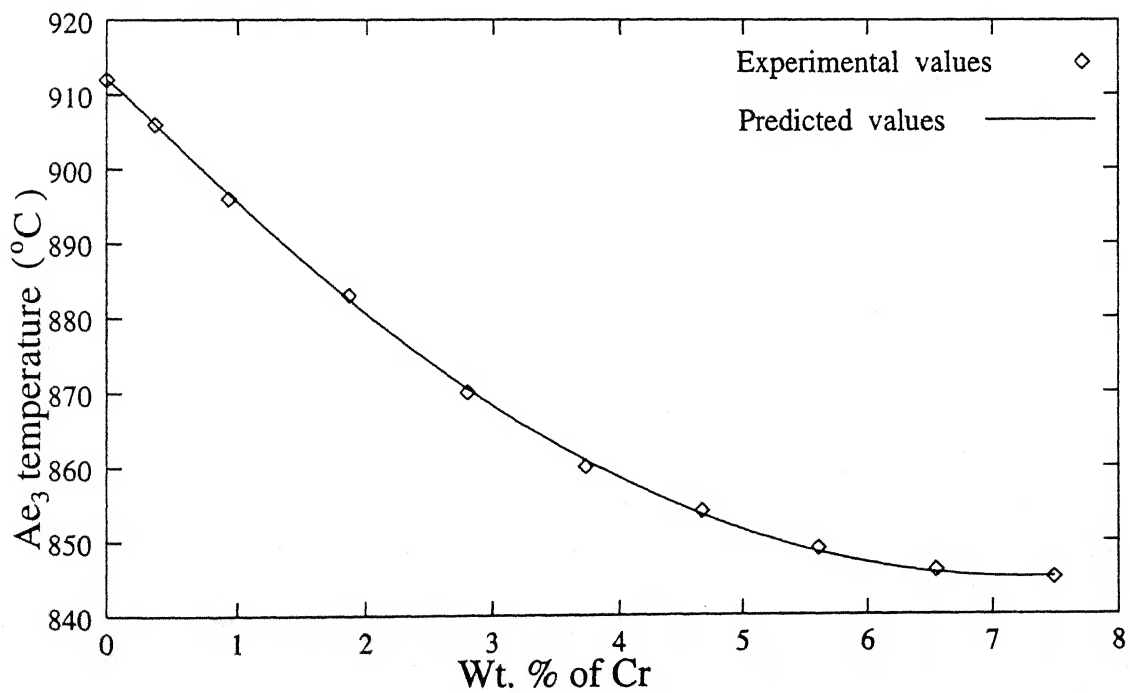
Figure 3.5: Experimental data and predicted Ae_3 temperature profile of Fe–Cr system
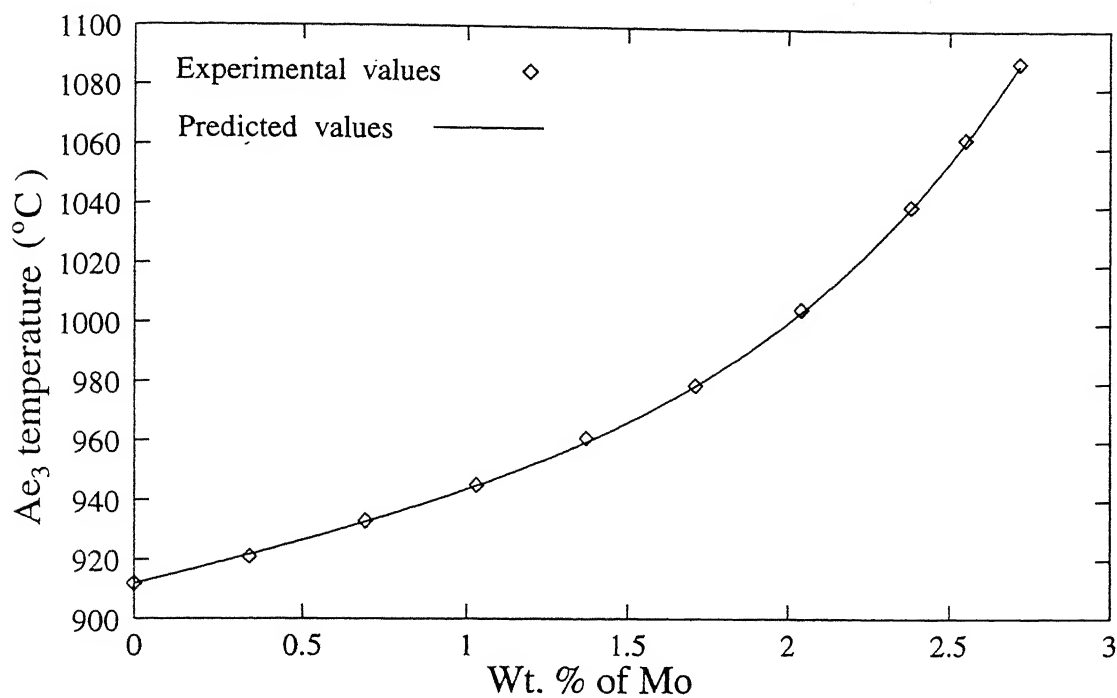
Figure 3.6: Experimental data and predicted Ae_3 temperature profile of Fe–Mo system
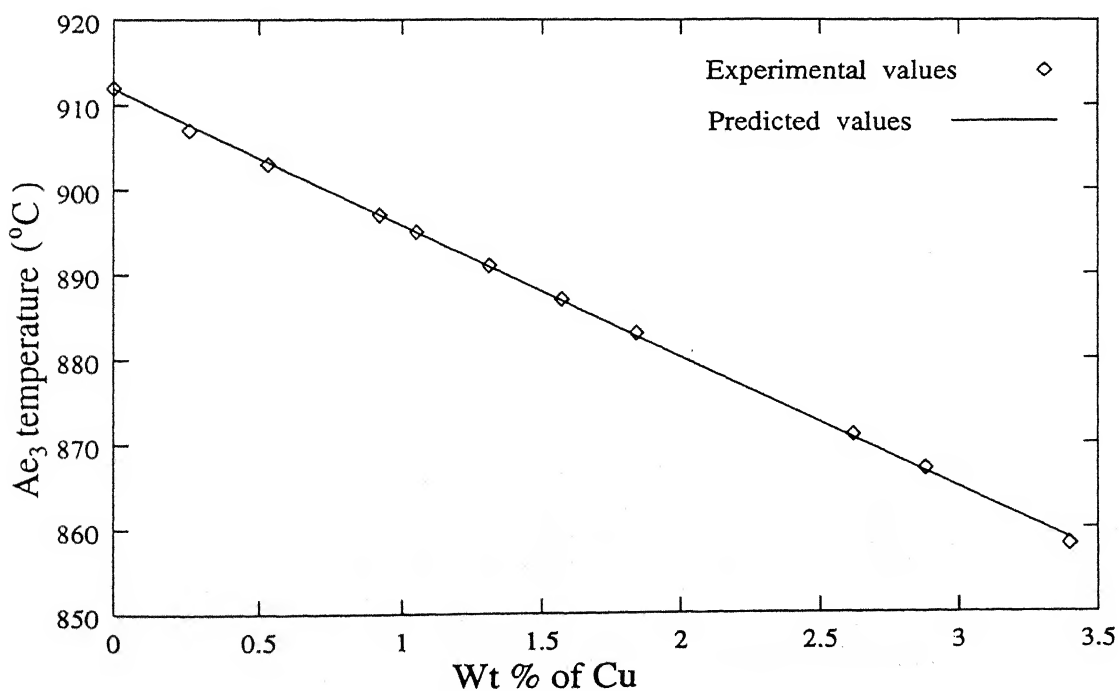
Figure 3.7: Experimental data and predicted Ae_3 temperature profile of Fe–Cu system

Chapter 4

MODEL FOR MULTICOMPONENT SYSTEM

4.1   Formulation of Model

Austenite in low alloy steels is a dilute solution of fcc iron and several alloying elements. The Ae_3 temperature of a steel depends on the composition of these alloying elements present in it. Hence, in principle, Ae_3 temperature can be estimated in terms of weight fractions of various alloying elements present in steel. In this analysis, the following alloying elements are considered: C, Mn, Si, Ni, Cr, Mo, and Cu.

Consider a steel containing 1 to n alloying elements and the solvent is o. The Ae_3 temperature (T_e) can be expressed as a function of its composition.

$$T_e = f(x_1, x_2, \ldots, x_i, \ldots, x_n) \tag{4.1}$$

where x_i is the weight fraction of ith alloying elements.

Assuming the relation to be a polynomial, Equation 4.1 can be expressed as :

$$T_e = \sum_{m_1} \cdots \sum_{m_i} \cdots \sum_{m_n} A_{m_1, m_2, \ldots, m_i, \ldots, m_n} X_1^{m_1} \ldots X_i^{m_i} \ldots X_n^{m_n} \tag{4.2}$$

where A represents the coefficients of polynomial and each m stands for all positive integers including zero.

By Taylor's series expansion around the composition $X_o \to 1$, and $X_1, \ldots, X_i, \ldots, X_m \to 0$

the coefficient of each term can be expressed as derivatives. So, A can be expressed as :

$$A_{m_1,\dots,m_i,\dots,m_n} = \frac{1}{\prod\limits_{1}^{n} m_i!} \left[\frac{\partial^r T_e}{\partial X_1^{m_1} \dots \partial X_i^{m_i} \dots \partial X_n^{m_n}} \right]_{X_o \to 1} \tag{4.3}$$

where, $r = \sum\limits_{1}^{n} m_i$

Equation 4.3 represents the rth order interaction coefficient. Thus, the Ae_3 temperature of steel can be expressed as :

$$T_e = A_0 + \sum_i A_i X_i + \sum_i A_{ii} X_i^2 + \frac{1}{2} \sum_i \sum_{k,\ k \neq i} A_{ik} X_i X_k + \dots \tag{4.4}$$

where i and k stand for alloying elements and A_0 is the Ae_3 temperature of pure iron.

The number of terms in the model depends on the desired accuracy in the results. The higher the number of terms, better is the predicted Ae_3 temperature. If only first order terms are retained, Equation 4.4 reduces to :

$$T_e = A_0 + A_1 X_1 + \dots + A_i X_i + \dots + A_n X_n \tag{4.5}$$

and if only upto second order terms are retained, it reduces to :

$$\begin{aligned} T_e &= A_0 + A_1 X_1 + \dots + A_i X_i + \dots + A_n X_n + A_{11} X_1^2 + \dots + A_{1i} X_1 X_i + \dots \\ &\quad + A_{1n} X_1 X_n + A_{22} X_2^2 + A_{23} X_2 X_3 + \dots + \dots + A_{nn} X_n^2 \end{aligned} \tag{4.6}$$

Similar expressions for T_e containing polynomial terms upto any desired order can be written.

4.2 Evaluation of the Coefficients of the Model

For evaluating the multicomponent model, a polynomial upto fourth order is considered. There are 330 terms in the model consisting of one zero order (or constant) term, 7 first order terms, 28 second order terms, 84 third order terms, and 210 fourth order terms. Out of these 330 terms, 28 terms belong to binary systems and rest 301 terms belong to multicomponent systems.

The zero order term or the constant term is taken to be 912^0C, the austenite to ferrite transformation temperature of pure iron. The 28 binary terms in this multicomponent model are replaced by the binary terms obtained earlier from the binary models. Even by

this substitution, the number of independent variables involved in the calculation is still fairly large (301 variables). Stepwise linear regression technique discussed in section 2.5 is used for evaluating the important parameters and their coefficients. The regression analysis is carried out on the multicomponent data. 109 data sets involving multicomponent steels are used for parameter estimation.

The number of variables retained after regression analysis depended on the significant levels, namely, α_1 and α_2, as defined in the calculation involved in the stepwise regression technique [19, 20, 21]. In the present work, the values of α_1 and α_2 are taken to be equal in accordance with the reasoning given by Draper & Smith [18]. Finally, the coefficients of the multicomponent model are evaluated for different sets of α_1 and α_2. It is observed that the number of variables increased with the values of significant levels, (i.e., α_1 and α_2).

A standard subroutine "RSTEP" available in IMSLibrary is used for evaluating the coefficients. Appendix–A shows the calling program.

Prior to this, a slightly different approach is tried in which the constants and binary terms in the multicomponent model are replaced by the binary values obtained by Arnab [17], and then a stepwise linear regression is carried out as discussed earlier for the evaluation of multicomponent terms. This model is given Appendix–B. This model when compared to the one discussed earlier is found to be statistically inferior. The statistical analysis is also presented in Appendix–B.

4.2.1 Coefficients of the Model

The regression analysis is carried out for different values of α_1 and α_2. The variables and their coefficients obtained by regression analysis, setting α_1 and α_2 as 0.01, 0.03, and 0.05, are shown in Table 4.1. The number of multicomponent terms in the equations are found to be 9, 10, and 12, respectively. It is noticed that the 9 variables which are present in the model by setting $\alpha_1 = 0.01 = \alpha_2$ are also present in the other two models. But, they contain few other terms in addition to those 9 variables. The equations so obtained from regression analysis are :

- Model for $\alpha_1 = \alpha_2 = 0.01$ (Model 1) :

$$
\begin{aligned}
T_e =\ & 912 - 660X_C^{0.88} + 454X_C^{1.11} - 40.84X_{Mn}^{0.83} + 14.45X_{Si}^{3.25} + 67.6X_{Si}^{1.05} \\
& -50.92X_{Ni}^{0.62} + 4.67X_{Cr}^{1.70} - 21.16X_{Cr}^{1.14} + 1.67X_{Mo}^{3.99} + 30.0X_{Mo}^{1.05} \\
& -16.25X_{Cu}^{0.97} + 66.09X_C X_{Ni} + 40.81X_C X_{Cr} + 284.9X_{Mn}X_{Si} \\
& +13.48X_C X_{Mn}^2 - 35.46X_{Mn}3X_{Si} - 48.24X_C X_{Mo}^3 - 17.39X_C^2 X_{Ni}^2 \\
& -1235X_C X_{Mn}X_{Si}^2 - 547.9X_{Mn}X_{Si}X_{Mo}^2
\end{aligned}
\tag{4.7}
$$

- Model for $\alpha_1 = \alpha_2 = 0.03$ (Model 2) :

$$
\begin{aligned}
T_e =\ & 912 - 660X_C^{0.88} + 454X_C^{1.11} - 40.84X_{Mn}^{0.83} + 14.45X_{Si}^{3.25} + 67.6X_{Si}^{1.05} \\
& -50.92X_{Ni}^{0.62} + 4.67X_{Cr}^{1.70} - 21.16X_{Cr}^{1.14} + 1.67X_{Mo}^{3.99} + 30.0X_{Mo}^{1.05} \\
& -16.25X_{Cu}^{0.97} + 69.41X_C X_{Ni} + 38.12X_C X_{Cr} + 312.7X_{Mn}X_{Si} \\
& +13.17X_C X_{Mn}^2 - 43.03X_{Mn}^3 X_{Si} - 48.74X_C X_{Mo}^3 - 18.14X_C^2 X_{Ni}^2 \\
& -1269X_C X_{Mn}X_{Si}^2 - 67.51X_{Mn}X_{Si}X_{Mo}^2 - 547.9X_{Mn}X_{Si}X_{Mo}^2
\end{aligned}
\tag{4.8}
$$

- Model for $\alpha_1 = \alpha_2 = 0.05$ (Model 3) :

$$
\begin{aligned}
T_e =\ & 912 - 660X_C^{0.88} + 454X_C^{1.11} - 40.84X_{Mn}^{0.83} + 14.45X_{Si}^{3.25} + 67.6X_{Si}^{1.05} \\
& -50.92X_{Ni}^{0.62} + 4.67X_{Cr}^{1.70} - 21.16X_{Cr}^{1.14} + 1.67X_{Mo}^{3.99} + 30.0X_{Mo}^{1.05} \\
& -16.25X_{Cu}^{0.97} + 69.31X_C X_{Ni} + 37.79X_C X_{Cr} + 312.8X_{Mn}X_{Si} \\
& +13.12X_C X_{Mn}^2 - 40.98X_{Mn}^3 X_{Si} - 50.33X_C X_{Mo}^3 - 18.22X_C^2 X_{Ni}^2 \\
& +8525X_C^2 X_{Mo}X_{Cu} - 1328X_C X_{Mn}X_{Si}^2 - 59.58X_{Mn}X_{Si}X_{Mo}^2 \\
& -548.5X_{Mn}X_{Si}X_{Mo}^2 - 1.05 \times 10^4 X_{Mn}X_{Si}X_{Mo}X_{Cu}
\end{aligned}
\tag{4.9}
$$

Table 4.1: Coefficients of the multicomponent terms present in the models

Variables	Coefficients for		
	$\alpha_1 = \alpha_2 = 0.01$	$\alpha_1 = \alpha_2 = 0.03$	$\alpha_1 = \alpha_2 = 0.05$
$X_C X_{Ni}$	66.09	69.41	69.31
$X_C X_{Cr}$	40.81	38.12	37.97
$X_{Mn} X_{Si}$	284.9	312.7	312.8
$X_C X_{Mn}^2$	13.48	13.17	13.12
$X_{Mn}^3 X_{Si}$	-35.46	-43.03	-40.98
$X_C X_{Mo}^3$	-48.28	-48.74	-50.33
$X_C^2 X_{Ni}^2$	-17.39	-18.14	-18.22
$X_C^2 X_{Mo} X_{Cu}$	—	—	8525
$X_C X_{Mn} X_{Si}^2$	-1235	-1269	-1328
$X_{Mn} X_{Si}^2 X_{Ni}$	—	-67.51	-59.58
$X_{Mn} X_{Si} X_{Mo}^2$	-547.9	-626.0	-548.5
$X_{Mn} X_{Si} X_{Mo} X_{Cu}$	—	—	-10500

Table 4.2: Predicted Ae_3 temperature and residue in multicomponent steels for model 2

Sl. No.	Weight% of alloying elements							Ae_3 temperature in ^{0}C		Residue in ^{0}C
	C	Mn	Si	Ni	Cr	Mo	Cu	Expt.	Pred.	
1	0.35	0.37	0.21	0.00	0.00	0.00	0.00	799.00	804.04	-5.04
2	0.47	0.57	0.20	0.00	0.00	0.00	0.00	771.00	778.11	-7.11
3	0.63	0.87	0.22	0.00	0.00	0.00	0.00	735.00	748.01	-13.01
4	0.35	1.85	0.19	0.00	0.00	0.00	0.00	776.00	779.60	-3.60
5	0.42	1.58	0.30	0.00	0.00	0.00	0.00	771.00	772.55	-1.55
6	0.37	0.68	0.21	3.41	0.00	0.00	0.00	732.00	743.77	-11.77
7	0.38	0.72	0.21	1.32	0.49	0.00	0.00	755.00	764.72	-9.72
8	0.35	0.80	0.24	0.00	0.00	0.25	0.00	796.00	809.31	-13.31
9	0.48	0.94	0.16	0.00	0.00	0.25	0.00	762.00	771.20	-9.20
10	0.33	0.53	0.27	0.00	0.90	0.18	0.00	796.00	815.43	-19.43
11	0.37	0.77	0.15	0.00	0.98	0.21	0.00	785.00	791.90	-6.90
12	0.44	0.95	0.23	0.00	0.93	0.21	0.00	773.00	786.31	-13.31
13	0.42	0.78	0.24	1.79	0.80	0.33	0.00	746.00	751.73	-5.73
14	0.36	0.63	0.19	1.84	0.00	0.23	0.00	757.00	763.55	-6.55
15	0.42	0.68	0.16	0.00	0.93	0.00	0.00	773.00	782.61	-9.61
16	0.30	0.80	0.29	0.54	0.56	0.21	0.00	787.00	800.34	-13.34
17	0.50	0.77	0.22	0.60	0.51	0.22	0.00	751.00	756.33	-5.33
18	0.44	0.90	0.25	0.44	0.54	0.22	0.00	779.00	768.09	10.91
19	0.50	0.77	0.23	0.60	0.50	0.21	0.00	757.00	756.83	0.17
20	0.35	0.37	0.21	0.06	0.05	0.00	0.07	800.00	795.30	4.70
21	0.54	0.46	0.20	0.00	0.00	0.00	0.00	756.00	765.23	-9.23
22	0.17	0.92	0.07	0.04	0.01	0.01	0.03	825.00	814.66	10.34
23	0.20	0.81	0.16	0.00	0.00	0.00	0.00	845.00	836.87	8.13
24	0.50	0.91	0.13	0.00	0.00	0.00	0.00	766.00	762.35	3.65
25	0.63	0.87	0.17	0.02	0.04	0.00	0.02	737.00	742.51	-5.51
26	0.64	1.13	0.09	0.00	0.00	0.00	0.00	744.00	732.73	11.27
27	0.20	1.88	0.30	0.03	0.04	0.02	0.04	816.00	828.85	-12.85
28	0.35	1.85	0.19	0.01	0.03	0.00	0.02	778.00	776.52	1.48
29	0.43	1.58	0.31	0.01	0.05	0.01	0.02	773.00	765.16	7.84
30	0.61	0.27	0.21	0.99	0.04	0.01	0.04	745.00	739.22	5.78

Table 4.2 : Continued

Sl. No.	Weight% of alloying elements							Ae_3 temperature in ^{0}C		Residue
	C	Mn	Si	Ni	Cr	Mo	Cu	Expt.	Pred.	in ^{0}C
31	0.56	0.26	0.21	1.97	0.04	0.00	0.02	732.00	738.78	-6.78
32	0.59	0.25	0.21	3.90	0.04	0.01	0.03	712.00	701.09	10.91
33	0.37	0.68	0.21	3.41	0.05	0.00	0.07	734.00	742.58	-8.58
34	0.10	0.52	0.28	5.00	0.07	0.03	0.00	774.00	771.64	2.36
35	0.40	0.52	0.28	5.00	0.07	0.03	0.00	714.00	715.35	-1.35
36	0.38	0.37	0.25	0.07	0.57	0.00	0.05	791.00	791.22	-0.22
37	0.42	0.68	0.16	0.07	0.93	0.00	0.05	782.00	773.87	8.13
38	0.33	0.45	0.28	0.06	1.97	0.02	0.04	807.00	802.85	4.15
39	0.11	0.38	0.44	0.15	5.46	0.42	0.00	839.00	846.68	-7.68
40	0.65	0.68	0.23	0.02	0.02	0.10	0.02	741.00	744.53	-3.53
41	0.26	0.87	0.29	0.03	0.06	0.26	0.00	824.00	834.21	-10.21
42	0.35	0.80	0.24	0.06	0.06	0.25	0.00	802.00	801.66	0.34
43	0.48	0.94	0.16	0.04	0.03	0.25	0.03	769.00	765.17	3.83
44	0.68	0.87	0.26	0.01	0.03	0.24	0.03	744.00	732.88	11.12
45	0.42	0.20	0.18	0.00	0.00	0.21	0.00	782.00	790.83	-8.83
46	0.40	0.42	0.19	0.06	0.13	0.53	0.07	802.00	781.34	20.66
47	0.36	0.17	0.16	0.00	0.00	0.82	0.00	800.00	800.85	-0.85
48	0.22	0.79	0.24	0.03	0.08	0.50	0.02	814.00	824.79	-10.79
49	0.40	0.57	0.03	3.49	0.00	0.01	0.00	724.00	715.29	8.71
50	0.41	0.60	0.03	3.51	0.00	0.21	0.00	718.00	718.07	-0.07
51	0.39	0.56	0.03	3.53	0.00	0.74	0.00	718.00	725.20	-7.20
52	0.50	0.23	0.53	0.02	0.05	0.00	0.02	780.00	780.77	-0.77
53	0.48	0.57	0.20	0.06	0.02	0.01	0.46	764.00	761.85	2.15
54	0.38	0.72	0.21	1.32	0.49	0.00	0.02	754.00	764.35	-10.35
55	0.11	0.45	0.18	3.33	1.52	0.03	0.00	782.00	764.43	17.57
56	0.33	0.53	0.27	0.00	0.90	0.18	0.00	800.00	815.43	-15.43
57	0.37	0.77	0.15	0.04	0.98	0.21	0.00	786.00	785.96	0.04
58	0.17	0.57	0.27	1.87	0.45	0.24	0.00	810.00	802.67	7.33
59	0.42	0.78	0.24	1.79	0.80	0.33	0.00	748.00	751.73	-3.73
60	0.15	0.63	0.28	1.90	0.05	0.24	0.00	794.00	812.62	-18.62
61	0.36	0.63	0.19	1.84	0.06	0.23	0.00	755.00	763.55	-8.55

Table 4.2 : Continued

Sl. No.	Weight% of alloying elements							Ae_3 temperature in ^0C		Residue in ^0C
	C	Mn	Si	Ni	Cr	Mo	Cu	Expt.	Pred.	
62	0.16	0.52	0.27	3.36	0.09	0.19	0.04	777.00	784.54	-7.54
63	0.18	0.79	0.21	0.52	0.56	0.19	0.00	838.00	821.57	16.43
64	0.30	0.80	0.29	0.54	0.55	0.21	0.00	792.00	800.39	-8.39
65	0.59	0.89	0.24	0.53	0.64	0.22	0.00	745.00	742.28	2.72
66	0.44	.90	0.25	0.45	0.54	0.22	0.00	775.00	767.89	7.11
67	0.24	0.94	0.47	0.30	0.34	0.14	0.00	844.00	843.21	0.79
68	0.10	1.63	0.21	0.00	0.00	0.41	0.00	864.00	849.99	14.01
69	0.63	0.87	0.17	0.02	0.04	0.00	0.02	736.00	742.51	-6.51
70	0.14	0.81	0.34	1.81	0.49	0.27	0.00	810.00	817.84	-7.84
71	0.16	0.60	0.27	1.92	0.06	0.27	0.00	800.00	807.60	-7.60
72	0.18	0.57	0.24	0.31	0.31	0.15	0.00	850.00	835.28	14.72
73	0.43	1.02	0.26	0.31	0.48	0.13	0.00	770.00	773.77	-3.77
74	0.45	0.89	0.31	0.59	0.66	0.12	0.00	773.00	766.03	6.97
75	0.50	0.77	0.23	0.60	0.50	0.21	0.00	755.00	756.83	-1.83
76	0.19	0.77	0.24	0.42	0.40	0.12	0.00	827.00	829.40	-2.40
77	0.18	0.67	0.17	1.07	0.00	0.00	0.00	824.00	803.22	20.78
78	0.19	0.75	0.18	1.04	0.00	0.00	0.00	823.00	803.44	19.56
79	0.17	1.65	0.16	1.07	0.00	0.00	0.00	800.00	789.19	10.81
80	0.21	0.75	0.18	1.08	0.48	0.00	0.00	811.00	793.84	17.16
81	0.21	0.78	0.19	1.09	0.99	0.00	0.00	800.00	791.15	8.85
82	0.22	0.77	0.19	1.08	1.91	0.00	0.00	786.00	783.19	2.81
83	0.18	0.65	0.12	1.09	0.00	0.26	0.00	811.00	796.74	14.26
84	0.18	0.75	0.71	1.07	0.00	0.00	0.00	855.00	853.39	1.61
85	0.37	0.77	0.15	0.04	0.98	0.21	0.00	787.00	785.96	1.04
86	0.22	0.79	0.24	0.03	0.08	0.50	0.02	812.00	824.79	-12.79
87	0.13	0.00	0.00	0.00	2.99	0.00	0.00	817.00	820.68	-3.68
88	0.41	0.00	0.00	0.00	2.99	0.00	0.00	787.00	782.63	4.37
89	0.13	0.00	0.00	0.00	0.00	0.39	0.00	875.00	860.50	14.50
90	0.40	0.00	0.00	0.00	0.00	0.38	0.00	795.00	791.45	3.55
91	0.12	3.08	0.00	0.00	0.00	0.00	0.00	765.00	764.09	0.91
92	0.37	3.14	0.00	0.00	0.00	0.00	0.00	725.00	729.89	-4.89

Table 4.2 : Continued

Sl. No.	Weight% of alloying elements							Ae_3 temperature in ^{0}C		Residue
	C	Mn	Si	Ni	Cr	Mo	Cu	Expt.	Pred.	in ^{0}C
93	0.11	0.00	0.00	3.28	0.00	0.00	0.00	775.00	772.89	2.11
94	0.37	0.00	0.00	3.04	0.00	0.00	0.00	733.00	741.10	-8.10
95	0.11	0.00	0.00	0.00	0.00	1.95	0.00	902.00	902.01	-0.01
96	0.46	2.94	0.00	0.00	0.00	0.00	0.00	730.00	722.89	7.11
97	0.22	5.01	0.00	0.00	0.00	0.00	0.00	730.00	739.55	-9.55
98	0.30	2.43	0.00	0.00	0.00	0.00	0.00	762.00	740.51	21.49
99	0.00	1.80	0.00	0.00	2.90	0.00	0.00	800.00	802.78	-2.78
100	0.00	1.70	0.00	0.00	2.80	0.00	0.00	800.00	807.00	-7.00
101	0.00	2.00	0.00	0.00	3.60	0.00	0.00	800.00	789.46	10.54
102	0.00	1.60	0.00	0.00	2.50	0.00	0.00	800.00	813.70	-13.70
103	0.00	3.30	0.00	0.00	5.50	0.00	0.00	750.00	738.93	11.07
104	0.00	3.20	0.00	0.00	4.40	0.00	0.00	750.00	748.15	1.85
105	0.00	3.30	0.00	0.00	5.70	0.00	0.00	750.00	738.09	11.91
106	0.16	0.00	0.00	0.00	2.40	0.00	0.00	829.00	817.72	11.28
107	0.17	0.00	0.00	0.00	3.16	0.00	0.00	820.00	811.67	8.33
108	0.14	0.00	0.00	0.00	3.83	0.00	0.00	807.00	814.63	-7.63
109	0.15	0.00	0.00	0.00	4.15	0.00	0.00	804.00	812.00	-8.00
110	0.00	0.00	0.00	0.00	0.00	0.00	0.00	912.00	912.00	0.00
111	0.05	0.00	0.00	0.00	0.00	0.00	0.00	882.00	881.05	0.95
112	0.11	0.00	0.00	0.00	0.00	0.00	0.00	856.00	856.56	-0.56
113	0.18	0.00	0.00	0.00	0.00	0.00	0.00	834.00	833.73	0.27
114	0.25	0.00	0.00	0.00	0.00	0.00	0.00	815.00	814.58	0.42
115	0.33	0.00	0.00	0.00	0.00	0.00	0.00	795.00	795.83	-0.83
116	0.40	0.00	0.00	0.00	0.00	0.00	0.00	782.00	781.50	0.50
117	0.47	0.00	0.00	0.00	0.00	0.00	0.00	769.00	768.76	0.24
118	0.55	0.00	0.00	0.00	0.00	0.00	0.00	756.00	755.81	0.19
119	0.60	0.00	0.00	0.00	0.00	0.00	0.00	749.00	748.48	0.52
120	0.66	0.00	0.00	0.00	0.00	0.00	0.00	740.00	740.38	-0.38
121	0.70	0.00	0.00	0.00	0.00	0.00	0.00	736.00	735.37	0.63
122	0.77	0.00	0.00	0.00	0.00	0.00	0.00	727.00	727.28	-0.28
123	0.00	0.49	0.00	0.00	0.00	0.00	0.00	890.00	889.41	0.59

Table 4.2 : Continued

Sl. No.	Weight% of alloying elements							Ae_3 temperature in ^{0}C		Residue
	C	Mn	Si	Ni	Cr	Mo	Cu	Expt.	Pred.	in ^{0}C
124	0.00	1.48	0.00	0.00	0.00	0.00	0.00	856.00	855.45	0.55
125	0.00	1.97	0.00	0.00	0.00	0.00	0.00	840.00	840.30	-0.30
126	0.00	2.46	0.00	0.00	0.00	0.00	0.00	826.00	825.79	0.21
127	0.00	2.95	0.00	0.00	0.00	0.00	0.00	811.00	811.76	-0.76
128	0.00	3.44	0.00	0.00	0.00	0.00	0.00	798.00	798.12	-0.12
129	0.00	3.94	0.00	0.00	0.00	0.00	0.00	785.00	784.55	0.45
130	0.00	4.43	0.00	0.00	0.00	0.00	0.00	771.00	771.52	-0.52
131	0.00	4.92	0.00	0.00	0.00	0.00	0.00	759.00	758.74	0.26
132	0.00	5.42	0.00	0.00	0.00	0.00	0.00	746.00	745.92	0.08
133	0.00	5.91	0.00	0.00	0.00	0.00	0.00	734.00	733.56	0.44
134	0.00	0.00	0.13	0.00	0.00	0.00	0.00	920.00	919.94	0.06
135	0.00	0.00	0.25	0.00	0.00	0.00	0.00	927.00	927.83	-0.83
136	0.00	0.00	0.38	0.00	0.00	0.00	0.00	936.00	936.80	-0.80
137	0.00	0.00	0.51	0.00	0.00	0.00	0.00	946.00	946.37	-0.37
138	0.00	0.00	0.63	0.00	0.00	0.00	0.00	956.00	955.98	0.02
139	0.00	0.00	0.76	0.00	0.00	0.00	0.00	968.00	967.60	0.40
140	0.00	0.00	0.89	0.00	0.00	0.00	0.00	980.00	980.97	-0.97
141	0.00	0.00	1.02	0.00	0.00	0.00	0.00	996.00	996.64	-0.64
142	0.00	0.00	1.14	0.00	0.00	0.00	0.00	1013.00	1013.72	-0.72
143	0.00	0.00	1.27	0.00	0.00	0.00	0.00	1035.00	1035.76	-0.76
144	0.00	0.00	1.53	0.00	0.00	0.00	0.00	1094.00	1094.19	-0.19
145	0.00	0.00	0.00	0.53	0.00	0.00	0.00	878.00	877.65	0.35
146	0.00	0.00	0.00	1.05	0.00	0.00	0.00	860.00	859.52	0.48
147	0.00	0.00	0.00	1.58	0.00	0.00	0.00	845.00	844.38	0.62
148	0.00	0.00	0.00	2.10	0.00	0.00	0.00	831.00	831.34	-0.34
149	0.00	0.00	0.00	2.62	0.00	0.00	0.00	819.00	819.48	-0.48
150	0.00	0.00	0.00	3.15	0.00	0.00	0.00	809.00	808.29	0.71
151	0.00	0.00	0.00	3.67	0.00	0.00	0.00	798.00	797.98	0.02
152	0.00	0.00	0.00	4.20	0.00	0.00	0.00	789.00	788.03	0.97
153	0.00	0.00	0.00	5.24	0.00	0.00	0.00	770.00	769.81	0.19
154	0.00	0.00	0.00	5.77	0.00	0.00	0.00	761.00	761.06	-0.06

Table 4.2 : Continued

Sl. No.	Weight% of alloying elements							Ae_3 temperature in ^{0}C		Residue
	C	Mn	Si	Ni	Cr	Mo	Cu	Expt.	Pred.	in ^{0}C
155	0.00	0.00	0.00	0.00	0.37	0.00	0.00	906.00	906.05	-0.05
156	0.00	0.00	0.00	0.00	0.93	0.00	0.00	896.00	896.65	-0.65
157	0.00	0.00	0.00	0.00	1.86	0.00	0.00	883.00	882.48	0.52
158	0.00	0.00	0.00	0.00	2.80	0.00	0.00	870.00	870.45	-0.45
159	0.00	0.00	0.00	0.00	3.73	0.00	0.00	860.00	860.88	-0.88
160	0.00	0.00	0.00	0.00	4.67	0.00	0.00	854.00	853.53	.0.47
161	0.00	0.00	0.00	0.00	5.61	0.00	0.00	849.00	848.49	0.51
162	0.00	0.00	0.00	0.00	6.55	0.00	0.00	846.00	845.69	0.31
163	0.00	0.00	0.00	0.00	7.49	0.00	0.00	845.00	845.10	-0.10
164	0.00	0.00	0.00	0.00	0.00	0.34	0.00	921.00	921.78	-0.78
165	0.00	0.00	0.00	0.00	0.00	0.69	0.00	933.00	932.90	0.10
166	0.00	0.00	0.00	0.00	0.00	1.03	0.00	945.00	945.13	-0.13
167	0.00	0.00	0.00	0.00	0.00	1.37	0.00	961.00	960.03	0.97
168	0.00	0.00	0.00	0.00	0.00	1.71	0.00	979.00	979.42	-0.42
169	0.00	0.00	0.00	0.00	0.00	2.04	0.00	1005.00	1004.77	0.23
170	0.00	0.00	0.00	0.00	0.00	2.38	0.00	1040.00	1040.43	-0.43
171	0.00	0.00	0.00	0.00	0.00	2.55	0.00	1063.00	1062.92	0.08
172	0.00	0.00	0.00	0.00	0.00	2.72	0.00	1089.00	1089.14	-0.14
173	0.00	0.00	0.00	0.00	0.00	0.00	0.26	907.00	907.60	-0.60
174	0.00	0.00	0.00	0.00	0.00	0.00	0.53	903.00	903.22	-0.22
175	0.00	0.00	0.00	0.00	0.00	0.00	0.92	897.00	897.01	-0.01
176	0.00	0.00	0.00	0.00	0.00	0.00	1.05	895.00	894.96	0.04
177	0.00	0.00	0.00	0.00	0.00	0.00	1.31	891.00	890.88	0.12
178	0.00	0.00	0.00	0.00	0.00	0.00	1.57	887.00	886.83	0.17
179	0.00	0.00	0.00	0.00	0.00	0.00	1.84	883.00	882.64	0.36
180	0.00	0.00	0.00	0.00	0.00	0.00	2.62	871.00	870.64	0.36
181	0.00	0.00	0.00	0.00	0.00	0.00	2.88	867.00	866.66	0.34
182	0.00	0.00	0.00	0.00	0.00	0.00	3.40	858.00	858.74	-0.74

Table 4.3: R^2 and R^2_{Adj} Values for three models

	R^2 values	R^2_{Adj} values
Model 1	0.9901	0.9889
Model 2	0.9910	0.9896
Model 3	0.9917	0.9905

4.3 Critical Appraisal of Regression Models

The various models corresponding to different α_1 and α_2 values are statistically evaluated for the best fit. The results of the statistical analysis for the three models are shown in Table 4.4. All the models show comparable statistical parameters. Hence, to select the best model out of these three models, additional statistical analysis, R^2 and R^2_{Adj} and F-test, are carried out.

4.3.1 Comparison of R^2 and R^2_{Adj} Values

The values of R^2 and R^2_{Adj} are given by the following expressions.

$$R^2 = 1 - \frac{RSS}{TSS} = 1 - \frac{\sum \epsilon_i^2}{\sum (Y_i - \bar{Y})^2} \tag{4.10}$$

$$R^2_{Adj} = 1 - \frac{\sum \epsilon_i^2/(N-K)}{\sum (Y_i - \bar{Y})^2/(N-1)} \tag{4.11}$$

where RSS = Residual sum of square

TSS = True sum of square

N = Number of data points

K = Number of parameters

$\bar{Y}$ = Average of Y_i

From Table 4.3 and Table 4.4, it is observed that model 1 is statistically inferior to other two models, and hence rejected. The R^2 and R^2_{Adj} values for model 2 and model 3 are nearly equal. So, to find the better one among these two models, F-test is conducted.

4.3.2 F-test for finding the best model

The F distribution is a continuous probability distribution. It has two parameters, ν_1 and ν_2, which are positive whole numbers. The F distribution of two independent variables having ν_1 and ν_2, as the degrees of freedom, respectively, is given by :

$$F_{(\nu_1,\nu_2)} = \frac{\chi_{(\nu_1)}^2}{\nu_1} \bigg/ \frac{\chi_{(\nu_2)}}{\nu_2} \qquad (4.12)$$

where $\chi_{(\nu_1)}^2$ and $\chi_{(\nu_2)}^2$ are independent variables.

The values of F distribution have been tabulated in standard statistical books, for different values of ν_1 and ν_2 at certain degrees of accuracy, α (also known as confidence level). Again

$$F_{(\nu_1,\nu_2,\alpha)} = \frac{1}{F_{(\nu_1,\nu_2,\alpha)}}$$

F-test can be done in term of number of restrictions. On simplification of the F^* expression the equation becomes :

$$F^* = \frac{(R_{UR}^2 - R_R^2)/m}{1 - R_{UR}^2/(N - K)}$$

where m = Number of restrictions

      K = Number of parameters in unrestricted model   Comparing the model 2 and

      N = Number of data points

model 3, it is observed that model 3 contain two extra terms than model 2. So, eliminating the extra terms in model 3, model 2 can be obtained.So, model 3 is the unrestricted equation and model 2 is the restricted equation, and the number of restrictions is two. To carry out the F-test for the best models, out of these two, following assumptions are made :

- H_0 : Both the models, i.e., model 2 and model 3, are statistically same

  (*null hypothesis*)

- H_a : Model 3 is statistically better than model 2

  (*alternate hypothesis*)

And if $F_{(m,N-K,\alpha)} \geq F^*$; conclude H_0

$\qquad\qquad\qquad < F^*$; conclude H_a

Assuming 0.95 confidence level, the value of F^* is found to be 8.55, and the value of $F_{(m,N-K,\alpha)}$ i.e., $F_{(2,159;0.95)}$ from the F distribution table is found to be 19.5, which is greater than 8.55. This shows that both the models perform well.

Model 3 contains two extra terms than that of model 2. Both the extra terms are of fourth order and contain X_{Cu}. The fourth order interaction coefficients for Cu are negligible. Model 2 containing lesser number of terms, makes the evaluation of Ae_3 temperature computationally easier, hence, accepted as the best model. A better symmetrical distribution of residues is also observed in case of model 2. Also the mean of the residues is almost zero for model 2. All these reasons goes in favour of selecting the model 2 as the best model.

Experimental versus predicted Ae_3 temperature curves of steels for the three models are shown in Figures 4.1, 4.4, and 4.5. The frequency distribution of residues and cumulative frequency distribution of residues are shown in Figures 4.2, 4.3, 4.6, and 4.7. More than 50% of the residues lie within ±1. Nearly 84% of the residues lie within ±10. All these observations enhance the acceptability of the models.

The error in the model prediction is presumed to be due to the inherent error in the experimental data itself. The experimental uncertainties in the measured Ae_3 temperature is discussed in section 2.3. Re-examination of the data for which the residues are more than ±10 is suggested. Chemical analysis should be carried out and the effect of impurities on Ae_3 temperature should be critically evaluated. Impurities like phosphorus and sulphur are proved to be notorious in this regard. According to Andrews [14], phosphorus influences the Ae_3 temperature to the extent of 700^0C per weight % of phosphorus.

4.4 Comparison with Existing Models

Table 4.3 shows various statistical values of the earlier models and the present model. From the table, it can be inferred that standard error in the present model is less compared to the existing ones. The correlation coefficient of the present model is also better. The number of terms in the present model is 22 which is higher than Arnab's [17] and Khaira's [15] models. A more symmetric frequency distribution of residue is obtained in the present model. The correlation coefficients for all binary systems is more than 0.999 (Table 3.5) for the present model. When multicomponent steels are considered, the correlation coefficient is found to be 0.97 as seen in Table 4.4. This shows that the model fits both multicomponent and binary systems satisfactorily.
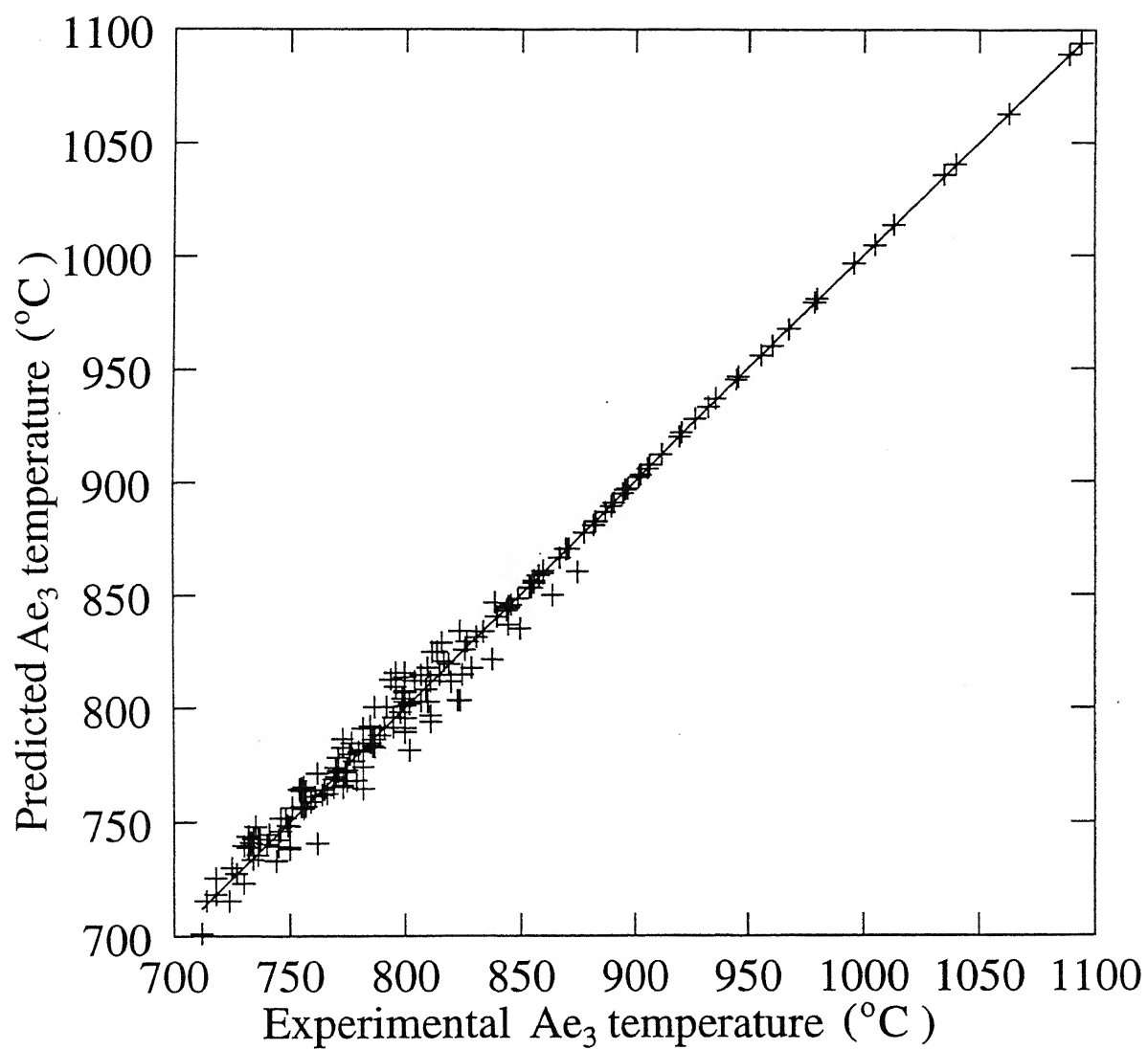
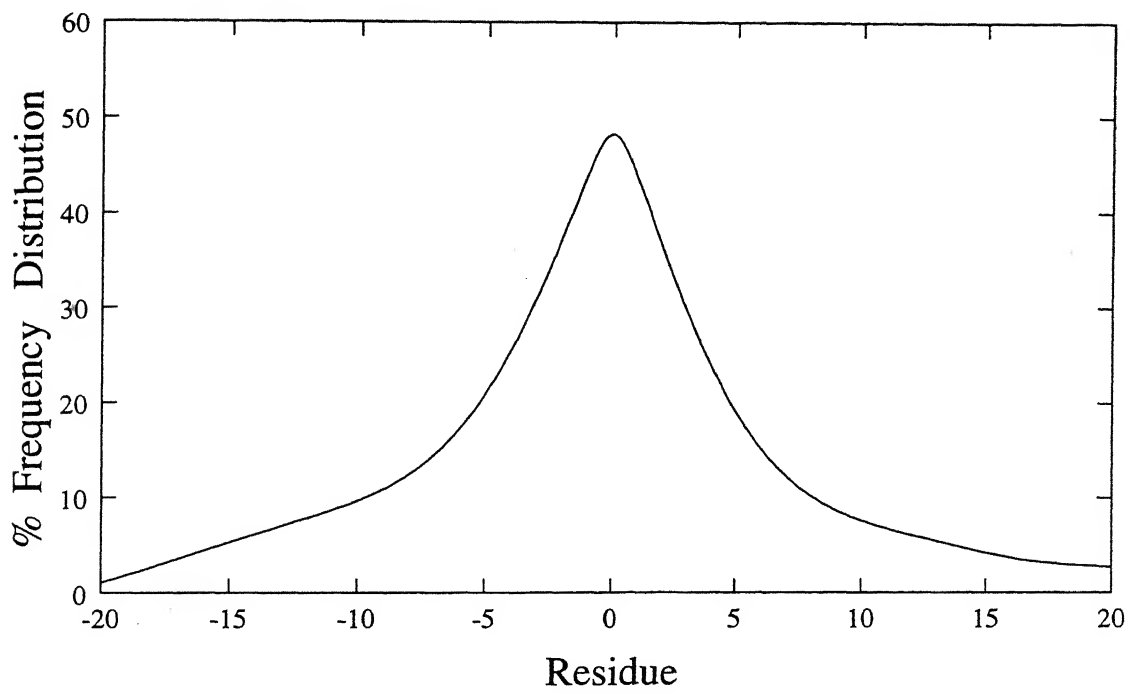Figure 4.1: Scattergram for model 2

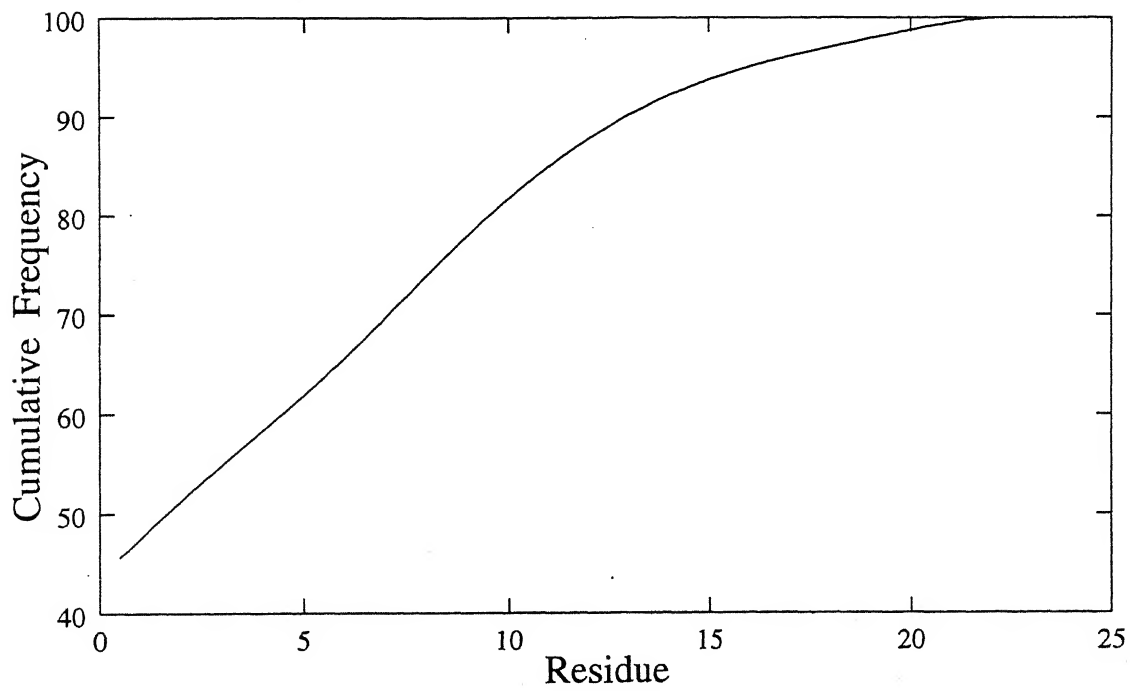Figure 4.2: Frequency distribution of residues for model 2

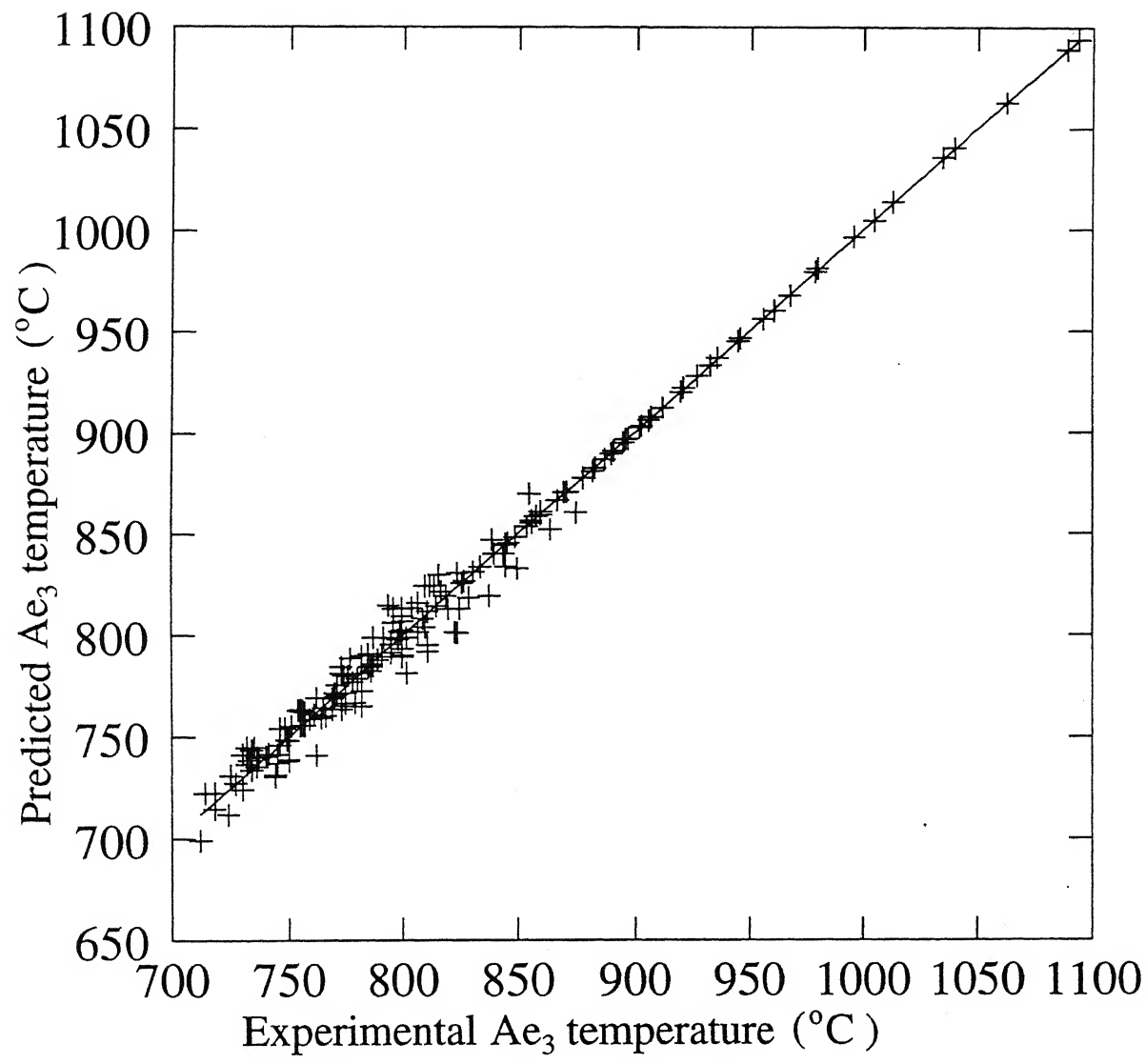Figure 4.3: Cumulative frequency distribution of residues for model 2

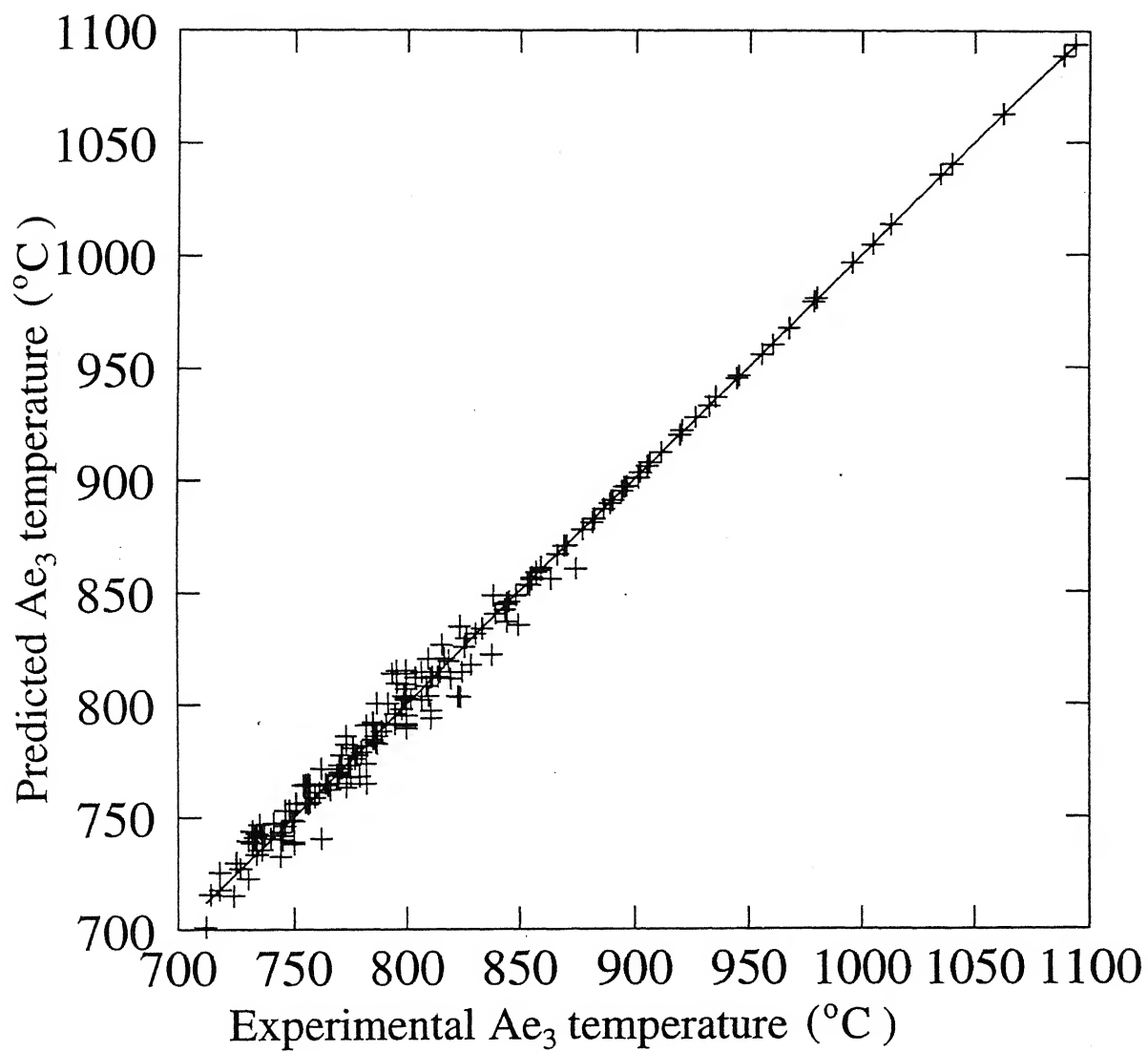Figure 4.4: Scattergram for model 1

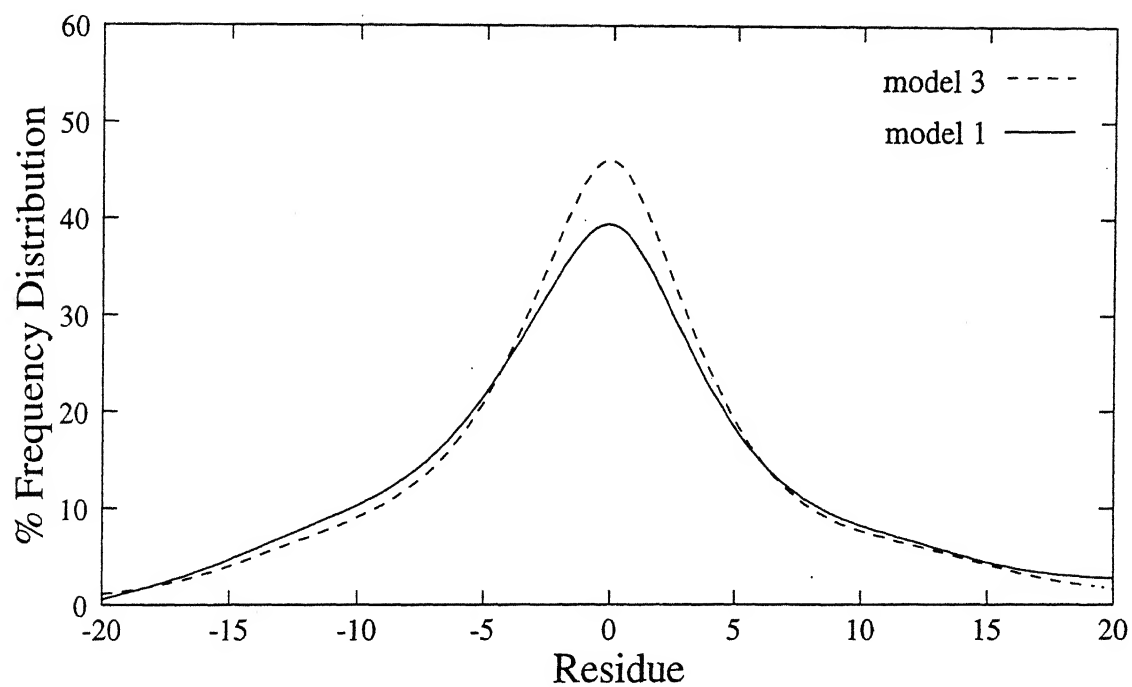Figure 4.5: Scattergram for model 3

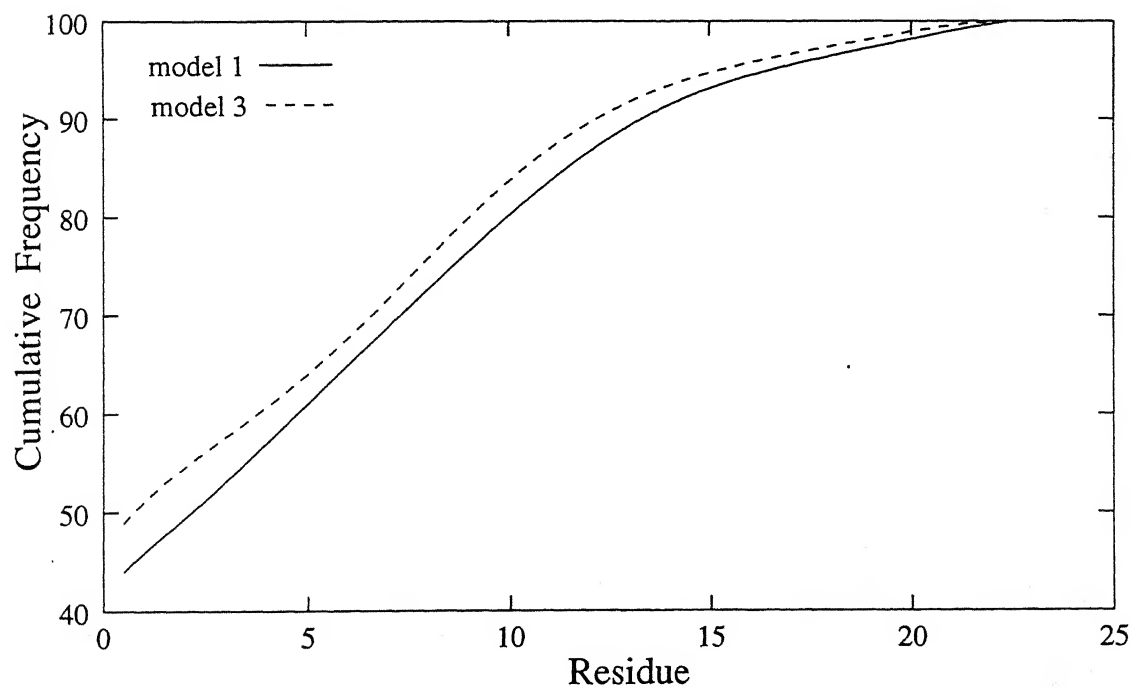Figure 4.6: Frequency distribution of residues for model 1 and model 3

Figure 4.7: Cumulative frequency distribution of residues for model 1 and model 3

Table 4.4: Statistical analysis of the results obtained by three models considering both binary and multicomponent steels

Statistical parameters	Multicomponent steels model for		
	$\alpha_1 = 0.01 = \alpha_2$	$\alpha_1 = 0.03 = \alpha_2$	$\alpha_1 = 0.05 = \alpha_2$
No. of steels	182	182	182
SSE	10606.13	9802.77	8837.09
SE	7.64	7.34	6.97
Mean Error	0.24	0.0012	-0.052
Min. Residue	-20.78	-19.43	-19.83
Max. Residue	22.63	21.49	21.58
Correlation Coefficients	0.9950453	0.9954084	0.9958596

Table 4.5: Statistical analysis of the results from different models for Ae_3 temperature

Statistical parameters	Present (model 2)	Arnab [17]	Manoj [16]	Khaira [15]	Baganis [7]	Andrews [14]	Grange
No. of steels	182	177	177	173	171	160	177
No. of terms	22	20	24	19	—	10	6
SE	7.34	9.5	8.9	9.0	13.8	19.2	33.3
Residue (max.)	21.49	24.88	34.79	20.5	50.1	85.1	203.6
Residue (min.)	-19.43	-23.54	-25.70	-22.5	-16.8	-76.8	-52.4
Correlation coefficients	0.9954	0.9911	0.9904	0.9920	0.9770	0.9610	0.909

- Fe–Mo : $T_e = 912 + 1.67X_{Mo}^{3.99} + 30.0X_{Mo}^{1.05}$

- Fe–Cu : $T_e = 912 - 16.25X_{Cu}^{0.97}$

These correlations are incorporated in a multicomponent model that correlates the Ae_3 temperature to the composition of alloying elements. This model unlike the earlier binary model contains the mutual interaction terms. A regression analysis of the data led to basically three models, each one differing by the levels of significance associated with them. In other words, the regression analysis is carried out several times with varying degrees of significance and only three models are retained solely on the consideration of number of terms involved in the model. The connotation of the significance level is merely a way of keeping and rejecting a given variable from the model.

The model equations are given below:

- Model for $\alpha_1 = \alpha_2 = 0.01$ (Model 1) :

$$
\begin{aligned}
T_e = {} & 912 - 660X_C^{0.88} + 454X_C^{1.11} - 40.84X_{Mn}^{0.83} + 14.45X_{Si}^{3.25} + 67.6X_{Si}^{1.05} \\
& -50.92X_{Ni}^{0.62} + 4.67X_{Cr}^{1.70} - 21.16X_{Cr}^{1.14} + 1.67X_{Mo}^{3.99} + 30.0X_{Mo}^{1.05} \\
& -16.25X_{Cu}^{0.97} + 66.09X_C X_{Ni} + 40.81X_C X_{Cr} + 284.9X_{Mn}X_{Si} \\
& +13.48X_C X_{Mn}^2 - 35.46X_{Mn}3X_{Si} - 48.24X_C X_{Mo}^3 - 17.39X_C^2 X_{Ni}^2 \\
& -1235X_C X_{Mn}X_{Si}^2 - 547.9X_{Mn}X_{Si}X_{Mo}^2
\end{aligned}
$$

- Model for $\alpha_1 = \alpha_2 = 0.03$ (Model 2) :

$$
\begin{aligned}
T_e = {} & 912 - 660X_C^{0.88} + 454X_C^{1.11} - 40.84X_{Mn}^{0.83} + 14.45X_{Si}^{3.25} + 67.6X_{Si}^{1.05} \\
& -50.92X_{Ni}^{0.62} + 4.67X_{Cr}^{1.70} - 21.16X_{Cr}^{1.14} + 1.67X_{Mo}^{3.99} + 30.0X_{Mo}^{1.05} \\
& -16.25X_{Cu}^{0.97} + 69.41X_C X_{Ni} + 38.12X_C X_{Cr} + 312.7X_{Mn}X_{Si} \\
& +13.17X_C X_{Mn}^2 - 43.03X_{Mn}^3 X_{Si} - 48.74X_C X_{Mo}^3 - 18.14X_C^2 X_{Ni}^2 \\
& -1269X_C X_{Mn}X_{Si}^2 - 67.51X_{Mn}X_{Si}X_{Mo}^2 - 547.9X_{Mn}X_{Si}X_{Mo}^2
\end{aligned}
$$

- Model for $\alpha_1 = \alpha_2 = 0.05$ (Model 3) :

$$
\begin{aligned}
T_e = {} & 912 - 660X_C^{0.88} + 454X_C^{1.11} - 40.84X_{Mn}^{0.83} + 14.45X_{Si}^{3.25} + 67.6X_{Si}^{1.05} \\
& -50.92X_{Ni}^{0.62} + 4.67X_{Cr}^{1.70} - 21.16X_{Cr}^{1.14} + 1.67X_{Mo}^{3.99} + 30.0X_{Mo}^{1.05} \\
& -16.25X_{Cu}^{0.97} + 69.31X_C X_{Ni} + 37.79X_C X_{Cr} + 312.8X_{Mn}X_{Si} \\
& +13.12X_C X_{Mn}^2 - 40.98X_{Mn}^3 X_{Si} - 50.33X_C X_{Mo}^3 - 18.22X_C^2 X_{Ni}^2 \\
& +8525X_C^2 X_{Mo}X_{Cu} - 1328X_C X_{Mn}X_{Si}^2 - 59.58X_{Mn}X_{Si}X_{Mo}^2 \\
& -548.5X_{Mn}X_{Si}X_{Mo}^2 - 1.05 \times 10^4 X_{Mn}X_{Si}X_{Mo}X_{Cu}
\end{aligned}
$$

These three models chosen predict the Ae_3 temperatures quite well, both for the binary as well as for the multicomponent steels. However, a careful analysis of the above three models reveals that in a statistical sense the second model is the most acceptable one.

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Appendix A

```
C**              *** STEPWISE LINEAR REGRESSION ANALYSIS OF ***

C**                    *** MULTICOMPONENT STEELS ***

         external  rstep,mxtxf,amach

         real  d,amach,aov,coef,cov,covs,hist,pin,pout,scale,tol
         integer  invoke,iprint,nca,istep,level,nforce,nobs,nstep

         dimension  d(109,8),c(109,302),cov(302,302),level(302),scale(302)
         dimension  hist(302),aov(13),coef(302,5),covs(302,302)

         nvar=302
         ndata=109

         open(unit = 1, file = 'p.data')

         read(1,*)((d(n,j),j = 1 , 8), n = 1 , 109)

         do n = 1 , 109
         c(n,302) = d(n,8) - (912.0 - 37979.0358*d(n,1)**0.88
     1       + 75345.245*d(n,1)**1.11 - 1867.0*d(n,2)**0.83
     1       + 1e+9*d(n,3)**3.92 + 8509.0*d(n,3)**1.05
```

```
   1        - 884.89*d(n,4)**0.62 + 11730.51*d(n,5)**1.70
   1        - 4031.96*d(n,5)**1.14 + 1.6e+8*d(n,6)**3.99
   1        + 3818.0*d(n,6)**1.05 - 1415.32*d(n,7)**0.97)
          enddo


C**        generating second degree polynomials


          do n = 1 , 109
            m = 1
            do i = 1 , 7
              do j = i+1 , 7
                c(n,m) = d(n,i) * d(n,j)
                m = m + 1
              enddo
            enddo
          enddo


C**        generating third degree polynomials


          do n = 1 , 109
            m = 22
            do i = 1 , 7
              do 20 j = 1 , 7
                if(j.eq.i) go to 20
                c(n,m) = d(n,j) * d(n,i)**2
                m = m + 1
   20         continue
            enddo
          enddo
C**


          do n = 1 , 109
```

```
        m = 64
        do i = 1 , 7
           do j = i+1 , 7
              do k = j+1 , 7
                 c(n,m) = d(n,k) * d(n,j) * d(n,i)
                 m = m+1
              enddo
           enddo
        enddo
     enddo


C**      generating fourth degree polynomials


        do n = 1 , 109
           m = 99
           do i = 1,7
              do 10 j = 1,7
                 if(j.eq.i) go to 10
                 c(n,m) = d(n,j) * d(n,i)**3
                 m = 1 + m
10            continue
           enddo
        enddo
C**


        do n = 1 , 109
           m = 141
           do i = 1 , 7
              do j = i+1 , 7
                 c(n,m) = d(n,j)**2 * d(n,i)**2
                 m = m + 1
              enddo
```

```
            enddo
        enddo
C**


        do n = 1 , 109
            m = 162
            do i = 1 , 7
                do 33 j = 1 , 7
                    if(j.eq.i) go to 33
                    do 34 k = j+1 , 7
                        if(k.eq.i) go to 34
                        c(n,m) = d(n,k) * d(n,j) * d(n,i)**2
                        m = m + 1
34                  continue
33              continue
            enddo
        enddo
C**


        do n = 1 , 109
            m = 267
            do i = 1 , 7
                do j = i+1 , 7
                    do k = j+1 , 7
                        do l = k+1 , 7
                            c(n,m) = d(n,l)*d(n,k)*d(n,j)*d(n,i)
                            m = m+1
                        enddo
                    enddo
                enddo
            enddo
        enddo
```

```
read(*,*)a,b

nca = 302
nra = 109

call mxtxf(nra,nca,c,nra,nca,cov,nca)

invoke = 0
datalevel /301*1,-1/
nforce = 0
nstep = -1
istep = 1
nobs = 109
pin = a
pout = b
tol = 100.0*amach(4)
iprint = 1

call RSTEP(invoke,nca,cov,nca,level,nforce,nstep,istep,nobs,pin,
1       pout,tol,iprint,scale,hist,iend,aov,coef,nca,covs,nca)

do i = 1,13
   write(*,*)aov(i)
enddo

stop
end
```

Appendix B

During the early stages of model development, Ae_3 temperature of steels are predicted by considering a polynomial model as described in the section 4.1 for multicomponent steels. For the binary terms, several models available in the literature are compared and Arnab's [17] models are found to be the best amongst all. Accordingly, these binary models are incorporated in the multicomponent model. Fixing the constant terms as 912^0C, the important multicomponent terms and their coefficients are evaluated using the stepwise linear regression over multicomponent data. The equation so obtained is given below :

$$
\begin{aligned}
T_e = \ & 912 - 660X_C^{0.88} + 454X_C^{1.11} - 38X_{Mn}^{0.92} + 71X_{Si}^{1.13} - 516X_{Ni}^{1.18} + 468X_{Ni}^{1.22} \\
& -196X_{Cr}^{1.34} + 180X_{Cr}^{1.37} + 1.13X_{Mo}^{4.09} + 29.4X_{Mo}^{1.24} - 24X_{Cu}^{0.96} + 83.95X_C X_{Mn} \\
& +79.48X_C X_{Ni} + 37.72X_C X_{Cr} + 305.1X_{Mn}X_{Si} - 82.15X_C^2 X_{Mn} \\
& -94.71X_{Mn}^2 X_{Si} - 893.5X_{Si}^2 X_C - 13.06X_{Ni}^2 X_C - 82.45X_{Mo}^2 X_C \\
& -284.3X_C X_{Mo}X_{Si} + 200.1X_{Si}^3 X_C + 1029X_C^2 X_{Si}^2 - 589.9X_{Si}^2 X_{Mn}X_{Mo}
\end{aligned}
\tag{B.1}
$$

Statistical analysis of the results obtained through this equation is performed. The maximum and minimum residues are found to be 26.5 and -21.2, respectively. Considering all the binary and multicomponent data, the standard error was 8.32. On this basis, the model turned out to be statistically better than the existing models. But, it suffers from the drawback that it does not predict the Ae_3 temperature satisfactorily in case of binary alloys having higher composition. So, in the next attempt the binary equations are developed considering the alloying elements over a wide range of composition.